



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁵ : C08G 65/10, 65/26, 65/32 C07D 307/08	A2	(11) International Publication Number: WO 94/09055 (43) International Publication Date: 28 April 1994 (28.04.94)
(21) International Application Number: PCT/US93/09808 (22) International Filing Date: 20 October 1993 (20.10.93) (30) Priority data: 07/964,313 21 October 1992 (21.10.92) US 08/021,368 23 February 1993 (23.02.93) US 08/093,243 16 July 1993 (16.07.93) US (60) Parent Applications or Grants (63) Related by Continuation US 07/964,313 (CIP) Filed on 21 October 1992 (21.10.92) US 08/021,368 (CIP) Filed on 23 February 1993 (23.02.93) US 08/093,243 (CIP) Filed on 16 July 1993 (16.07.93) (71) Applicant (for all designated States except US): E.I. DU PONT DE NEMOURS AND COMPANY [US/US]; 1007 Market Street, Wilmington, DE 19898 (US).		(72) Inventors; and (75) Inventors/Applicants (for US only) : DRYSDALE, Neville, Everton [JM/US]; 227 Welch Tract Road, Newark, DE 19702-1026 (US). BOCKRATH, Richard, Edmund [US/US]; 2314 West 17th Street, Wilmington, DE 19806-1331 (US). (74) Agents: GEIGER, Kathleen, W. et al.; E.I. du Pont de Nemours and Company, Legal/Patent Records Center, 1007 Market Street, Wilmington, DE 19898 (US). (81) Designated States: JP, KR, US , European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>Without international search report and to be republished upon receipt of that report.</i>
(54) Title: POLYMERIZATION OF, AND DEPOLYMERIZATION TO, CYCLIC ETHERS USING SELECTED METAL COMPOUND CATALYSTS (57) Abstract <p>A process for polymerizing oxiranes, oxetanes, oxepanes, dioxolanes, trioxanes, and tetrahydrofurans to their respective polymers by contacting them with a selected metal compound is disclosed; and also a process for depolymerizing polytetrahydrofurans to monomeric tetrahydrofurans by contacting the polymer with a selected metal compound at a temperature of about 100 °C to about 250 °C.</p>		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	FR	France	MR	Mauritania
AU	Australia	GA	Gabon	MW	Malawi
BB	Barbados	GB	United Kingdom	NE	Niger
BE	Belgium	GN	Guinea	NL	Netherlands
BF	Burkina Faso	GR	Greece	NO	Norway
BG	Bulgaria	HU	Hungary	NZ	New Zealand
BJ	Benin	IE	Ireland	PL	Poland
BR	Brazil	IT	Italy	PT	Portugal
BY	Belarus	JP	Japan	RO	Romania
CA	Canada	KP	Democratic People's Republic of Korea	RU	Russian Federation
CF	Central African Republic	KR	Republic of Korea	SD	Sudan
CG	Congo	KZ	Kazakhstan	SE	Sweden
CH	Switzerland	LJ	Liechtenstein	SI	Slovenia
CI	Côte d'Ivoire	LK	Sri Lanka	SK	Slovak Republic
CM	Cameroon	LU	Luxembourg	SN	Senegal
CN	China	LV	Latvia	TD	Chad
CS	Czechoslovakia	MC	Monaco	TG	Togo
CZ	Czech Republic	MG	Madagascar	UA	Ukraine
DE	Germany	ML	Mali	US	United States of America
DK	Denmark	MN	Mongolia	UZ	Uzbekistan
ES	Spain			VN	Viet Nam
FI	Finland				

TITLE

POLYMERIZATION OF, AND
DEPOLYMERIZATION TO, CYCLIC ETHERS
USING SELECTED METAL COMPOUND CATALYSTS

5

FIELD OF THE INVENTION

This invention concerns the polymerization of
oxiranes, oxetanes, oxepanes, 1,3-dioxolanes,
1,3,5-trioxanes, and tetrahydrofurans to linear
polyethers, and the depolymerization of polytetra-
hydrofurans to tetrahydrofurans, both catalyzed by
selected metal compounds.

BACKGROUND OF THE INVENTION

Cyclic ethers are polymerized by various means to
give products of widespread utility. For instance,
ethylene oxide is polymerized to polyethylene oxide
which is useful, in lower molecular weight grades, for
ceramics (as a binder), cosmetics, lubricants,
polyurethanes; and in higher molecular weight grades,
for packaging film, denture adhesives, lubricants,
flocculation and for other articles and products.
Tetrahydrofuran (THF) is polymerized to poly(tetra-
methylene ether) glycol which is useful in the
preparation of Spandex fibers; polyurethane resins which
are useful in elastomeric parts; and thermoplastic
elastomers which are useful for molding various
mechanical parts. Therefore, improved methods of making
these polymers are sought. Also useful are methods of
depolymerizing the polyethers to useful products, such
as the cyclic ethers from which they were originally
made. Such depolymerizations allow for the recycle of
off specification or used polyethers to useful products
such as polyethers; thereby reducing waste.

U.S. Patent 3,842,019 describes the polymerization
of oxiranes and other small ring compounds by a presumed
cationic mechanism, using as the catalyst the

decomposition products of metal perfluoroalkyl-sulfonates. These catalysts are described as "latent", that is no reaction occurs until the metal salt is decomposed. The reactions reported are relatively slow, even at elevated temperatures.

U.S. Patents 5,084,586 and 5,124,417 describe the cationic polymerization of various monomers, including cyclic ethers, using onium cations, whose corresponding anions are fluororalkylsulfatometallates. Onium ion catalyzed cationic polymerizations are well known, and there is no mention in these patents of the use of metal salts not containing onium ions, such as metal triflates, as catalysts for the polymerization of cyclic ethers.

Japanese Patent Application 51-82397 describes the polymerization of tetrahydrofuran using a combination of fluorosulfonic acid and a carboxylic acid as catalysts. No mention is made of metal salts, such a metal triflates as catalysts.

J. S. Hrkach, et al., *Macromolecules*, vol. 23, p. 4042-4046 (1990) describe the polymerization of tetrahydrofuran using trimethylsilyl trifluoromethanesulfonate as the initiator. No mention is made of any other triflates as catalysts for this polymerization.

German Patent Application 2,459,163 describes the polymerization of THF using a combination of ferric chloride and carboxylic anhydride as catalyst.

G. A. Olah, et al., *J. Appl. Polym. Sci.*, Vol. 45, 1355-1360 (1992) describe the use of boron, aluminum and gallium tris(triflate) to catalyze the polymerization of THF.

S. L. Borkowsky, et al., *Organometal.*, Vol. 10, p. 1268-1274 (1991) report that certain zirconium complexes can initiate the polymerization of

tetrahydrofuran. No mention is made of zirconium perfluoroalkylsulfonates, or of copolymers.

T. Misaki, et al., Nippon Kagaku Kaishi, p. 168-174 (1973) report on the polymerization of THF using a combination of metal acetylacetonates and acetyl chloride.

None of the metal compounds herein disclosed as catalysts are mentioned in the above references.

SUMMARY OF THE INVENTION

10 This invention concerns a process for the polymerization of cyclic ethers, comprising, contacting one or more oxiranes, oxetanes, tetrahydrofurans, oxepanes, 1,3-dioxolanes or 1,3,5-trioxanes with a compound of the formula $MZ_s \cdot Q_t$, and an accelerator
15 selected from the group consisting of carboxylic acids whose pKa in water is less than 6, carboxylic anhydrides and acyl halides, wherein:

M is a metal selected from the group consisting of cobalt, vanadium, niobium, tungsten, strontium, barium, scandium, yttrium, the rare earth metals, titanium, zirconium, hafnium, chromium, molybdenum, tantalum, rhenium, iron, ruthenium, osmium, rhodium, iridium, palladium, platinum, silver, gold, zinc, cadmium, mercury, aluminum, gallium, indium, thulium, germanium, tin, lead, arsenic, antimony and bismuth;

at least one of Z is an anion of the formula $^{-}OSO_2R^5$, wherein R^5 is perfluoroalkyl containing 1 to 12 carbon atoms or part of a fluorinated polymer wherein the carbon atoms alpha and beta to the sulfonate group are together bonded to at least four fluorine atoms, or tetraphenylborate, and the remainder of Z is oxo or one or more monovalent anions;

s is 2 when M is strontium, barium, cobalt, rhodium, iridium, palladium, platinum, chromium, zinc, cadmium or mercury;

s is 3 when M is scandium, yttrium, a rare earth metal, arsenic, antimony, bismuth, gold, iron, ruthenium, osmium, aluminum, gallium, indium or thulium;

s is 4 when M is titanium, zirconium, hafnium, molybdenum, germanium, tin, or lead;

s is 5 when M is rhenium, vanadium, niobium or tantalum;

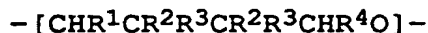
s is 6 when M is tungsten;

Q is a neutral ligand;

t is 0 or an integer of 1 to 6; and

provided that each oxo group present counts as two of s.

This invention also involves a process for the depolymerization of a polyether to a tetrahydrofuran, comprising, contacting at a temperature of about 100°C to about 250°C, a polymer consisting essentially of one or more repeat units of the formula



with a compound of the formula $\text{MZ}_s \cdot \text{Q}_t$, wherein:

each R^1 , R^2 , R^3 and R^4 is independently hydrogen or hydrocarbyl containing 1 to 20 carbon atoms;

M is a metal selected from the group consisting of cobalt, vanadium, niobium, tungsten, strontium, barium, scandium, yttrium, the rare earth metals, titanium, zirconium, hafnium, chromium, molybdenum, tantalum, rhenium, iron, ruthenium, osmium, rhodium, iridium, palladium, platinum, silver, gold, zinc, cadmium, mercury, aluminum, gallium, indium, thulium, silicon, germanium, tin, lead, arsenic, antimony and bismuth;

at least one of Z is an anion of the formula $-\text{OSO}_2\text{R}^5$, wherein R^5 is perfluoroalkyl containing 1 to 12

carbon atoms or part of a fluorinated polymer wherein the carbon atoms alpha and beta to the sulfonate group are together bonded to at least four fluorine atoms, or tetraphenylborate, and the remainder of Z is oxo or one
5 or more monovalent anions;

s is 2 when M is strontium, barium, cobalt, rhodium, iridium, palladium, platinum, chromium, zinc, cadmium or mercury;

s is 3 when M is scandium, yttrium, a rare
10 earth metal, arsenic, antimony, bismuth, gold, iron, ruthenium, osmium, aluminum, gallium, indium or thulium;

s is 4 when M is titanium, zirconium, hafnium, molybdenum, silicon, germanium, tin, or lead;

s is 5 when M is rhenium, vanadium, niobium or
15 tantalum;

s is 6 when M is tungsten;

Q is a neutral ligand;

t is 0 or an integer of 1 to 6;

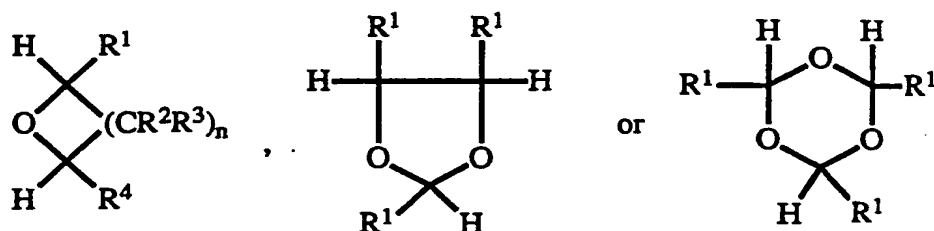
and provided that each oxo group present counts as
20 two of s.

DETAILS OF THE INVENTION

In the polymerization process described herein one or more cyclic ethers, oxiranes, oxetanes, 1,3-dioxolanes, 1,3,5-trioxanes, or tetrahydrofurans are
25 polymerized to form a polyether. Oxirane (more commonly called epoxide) is herein given its usual structure, a saturated three membered ring containing two carbon atoms and one oxygen atom. Oxetane is also given its common meaning, a saturated four membered ring
30 containing three carbon atoms and one oxygen atom. The term oxepane means a saturated seven membered ring containing six carbon atoms and one oxygen atoms. The term 1,3-dioxolane means a saturated five membered ring which contains two oxygen atoms separated by 1 carbon
35 atom. The term 1,3,5-trioxane means a six membered ring

containing 3 oxygen atoms in which the oxygen atoms and carbons atoms are alternated. All of these terms include compounds containing those ring systems which are substituted with hydrocarbyl or hydrocarbylene groups containing 1 to 20 carbon atoms. The hydrocarbylene groups may form carbocyclic rings, which include bicyclic, tricyclic, etc., systems. By a hydrocarbylene group herein is meant a divalent radical containing carbon and hydrogen which is part of a carbocyclic ring.

Preferred cyclic ethers have the formula



wherein n is 2 or 4 and each R^1 , R^2 , R^3 and R^4 is independently hydrogen or hydrocarbyl containing 1 to 20 carbon atoms. Some of these cyclic ethers polymerize to give repeat units of the formula $-\text{CHR}^1(\text{CR}^2\text{R}^3)_n\text{CHR}^4\text{O}-$. In a more preferred cyclic ether all of R^1 , R^2 , R^3 and R^4 are hydrogen. In another more preferred cyclic ether where $n=2$, R^1 , one of R^2 , both of R^3 and R^4 are hydrogen, and the remaining R^2 is alkyl containing 1-4 carbon atoms, especially preferably the remaining R^2 is methyl. By hydrocarbyl herein is meant a univalent radical containing carbon and hydrogen.

The polymerization is run in the presence of an accelerator. Suitable accelerators are carboxylic anhydrides, acyl halides, and carboxylic acids with a pK_a of less than about 6 in water.

By a carboxylic anhydride is meant a compound containing the grouping $-\text{C}(\text{O})\text{O}(\text{O})\text{C}-$, wherein the free

valencies are to other carbon atoms. A preferred carboxylic anhydride is an anhydride of an alkyl carboxylic acid or a halogen substituted alkyl carboxylic acid, and particularly preferred anhydrides
5 are acetic anhydride and trifluoroacetic anhydride.

By an acyl halide is meant a compound containing the grouping $-C(O)X$, where X is chlorine or bromine and the free valence is to another carbon atom. In preferred acyl halides, X is chlorine. Preferred acyl
10 halides are alkyl acyl halides, and especially preferred are acetyl halides, more preferably acetyl chloride.

By a carboxylic acid is meant a compound containing the grouping $-C(O)OH$, wherein the free valence is to another carbon atom. Preferred carboxylic acids have a
15 pKa of less than 5 in water. Useful carboxylic acids include, but are not limited to acetic, trifluoroacetic, chloroacetic, benzoic, trichloroacetic, p-nitrobenzoic, butyric, formic, cyanoacetic, nitropropionic, acrylic, methacrylic, naphthoic acids, N-acetylglycine and
20 N-acetyltryptophan. Preferred carboxylic acids are trifluoroacetic, acetic, formic, cyanoacetic, nitropropionic, acrylic, methacrylic acids, N-acetyl-glycine and N-acetyltryptophan.

When carboxylic anhydride is present one half or
25 more of the end groups are carboxylic esters. As is known to the artisan, these may be hydrolyzed to hydroxyl groups by reaction with water, preferably in the presence of a catalyst, such as a strong acid (sulfuric acid for instance) or a strong base (such as
30 NaOH). The proportion of acetate ends increases the longer the polymerization is allowed to proceed. Although the polymeric diol is often the desired product (it can be used to make other polymers, such as polyurethanes and polyesters), the half ester or diester

is also useful, as in relatively low molecular polymers which can be used as solvents.

When an acyl halide is used as the accelerator, the end groups are usually ester on one end, and the halide, X, on the other. Thus the complete formula for such a polymer could be $X-[CHR^1(CR^2R^3)_nCHR^4O]-C(O)Y$, where Y is the group to which the acyl group of the acyl halide was bound. Such polymers are useful as intermediates for the preparation of polymers containing different functional groups. For example, the ester may be hydrolyzed to a hydroxyl group, and the halide may be reacted to form another functional group such as nitrile. If a bis(acyl halide), $X(O)CYC(O)X$, is used as the accelerator, the product of the polymerization will be a polyether with halide (X) end groups which contains two internal ester groups, and may have the formula $X-[CHR^1(CR^2R^3)_nCHR^4O]-C(O)YC(O)-[OCHR^1(CR^2R^3)_nCHR^4]-X$. Useful bis(acyl halides) include adipoyl chloride, terephthaloyl chloride, and diglycolyl chloride $[Cl(O)CCH_2OCH_2C(O)Cl]$.

When a carboxylic acid is used as the accelerator, both end groups are usually mostly ester. Thus the complete formula for such a polymer could be $YO-[CHR^1(CR^2R^3)_nCHR^4O]-C(O)Y$, where Y is the group to which the acyl group of the carboxylic acid was bound.

An important consideration in the preparation of polyethers is the number average molecular weight (M_n) of the polyether and its molecular weight distribution. When the polyether is to be used as a monomer in the preparation of another polymer (usually in the diol form), it is often preferred that the M_n of the polyether be in the range of about 400 to about 20,000, preferably about 500 to about 5,000.

The catalyst may be yttrium or rare earth compound of the formula MZ_3 where M is a trivalent ion of

yttrium, or one of the rare earths, lanthanum, cerium, praeseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, and lutetium.

5 Preferred metals, M, are strontium, scandium yttrium, the rare earth metals, titanium, zirconium, hafnium, vanadium, niobium, tantalum, chromium, molybdenum, tungsten, rhenium, iron, ruthenium, palladium, copper, gold, zinc, tin and bismuth. More
10 preferred metals are yttrium, the rare earth metals, and scandium. Especially preferred metals are yttrium, ytterbium, dysprosium, erbium, neodymium, lanthanum, and scandium. Another preferred metal is "mischmetall" (sometimes also called "didymium"), which is a mixture
15 of rare earth metals as obtained from the ore.

It is believed monovalent anions that are relatively nonnucleophilic are useful as Z. Examples of such anions are tetraphenylborate, $^{-}\text{OSO}_2\text{R}^5$, wherein R^5 is perfluoroalkyl, or wherein R^5 is part of a fluorinated
20 polymer wherein the carbon atoms alpha and beta to a sulfonate group are together bonded to at least 4 fluorine atoms (as in $^{-}\text{CF}_2\text{CF}_2\text{OSO}_2^{-}$). It is preferred if R^5 is perfluoroalkyl. In a particularly preferred R^5 is trifluoromethyl, and the anion is herein called
25 "triflate".

Generally speaking, any metallic compound in which the correct metal in the correct oxidation state (see above) is present and bonded to a triflate or similar anion will be a catalyst. Such a compound must of
30 course be reasonably stable during the polymerization (or depolymerization, see below), or decompose to another compound which is still a triflate (or similar anion) compound of the metal in the correct oxidation state. It has been found that, in general, the greater
35 the number of triflate groups bonded to the metal

cation, the more active the metal compound will be as a catalyst. It is preferred if half or more of the anions (Z) bound to each metal cation is triflate or a similar anion.

5 The metal catalysts may optionally contain one or more neutral ligands coordinated to the metal. By a neutral ligand is meant a neutral compound that can coordinate with the catalysts, usually the metal cation. Neutral ligands include water, and ethers such as
10 dimethyl ether and tetrahydrofuran. Useful compounds containing neutral ligands include bis(n-cyclopentadienyl)tetrahydrofuran-bis(trifluoromethanesulfonato)-zirconium and bis(n-cyclopentadienyl)tetrahydrofuran-bis(trifluoromethanesulfonato)hafnium.

15 The metals catalysts may contain other anions than triflate and similar anions, and tetrafluoroborate, although at least one of triflate or tetrafluoroborate anions must be present. Some other useful anions are alkoxide, particularly lower alkoxide containing 1-4
20 carbon atoms, acetylacetonate, cyclopentadieneide, pentamethylcyclopentadieneide, t-butylacetylacetonate, and halide. It is preferred if all of the anions are triflate.

In general, the higher the molar ratio of metal
25 compound to cyclic ether monomer originally present, the lower the molecular weight of the resulting polyether will be. Similarly, the higher the ratio of accelerator (if present) to monomer originally present, the lower the molecular weight of the polyether will be. It is
30 believed the effects of these two ratios are cumulative. For these effects see Examples 7 and 8.

The polymerization may be run at a temperature of about -80°C to about 130°C. If this temperature is above the boiling point of the cyclic ether monomer, a
35 pressure vessel may be used. A preferred temperature is

ambient to the boiling point of the monomer, or 110°C, whichever is lower. An inert solvent such as di-n-butyl ether, diethyl ether or toluene may be used, but it is preferred if solvents are not present. Protic compounds
5 such as water, methanol and ethanol should preferably not be present, and it is convenient to exclude them by drying the starting materials and keeping the process under an inert dry gas such as nitrogen. As in most chemical processes, the ingredients should be mixed at
10 least initially. Continued agitation is preferred to assure that the process materials remain well mixed, and to avoid overheating. The polymerization is mildly exothermic. If the polymerization temperature goes up appreciably, refluxing of the monomer may be used to
15 help cool the process.

The polymers produced often have polydispersities significantly less than 2, which is possibly indicative of a "Living polymerization". Also indicative of this is the fact that as the polymerization proceeds, the
20 molecular weight, particularly the number average molecular weight, increases.

This invention is also concerned with the depolymerization of a polymer consisting essentially of the repeat unit $-[\text{CHR}^1\text{CR}^2\text{R}^3\text{CR}^2\text{R}^3\text{CHR}^4\text{O}]-$ wherein R^1 , R^2 ,
25 R^3 , and R^4 are defined above, and preferred combinations are as given above for the polymerization process when $n=2$. A catalyst designated $\text{MZ}_s\cdot\text{Q}_t$ is used, wherein M, S, Q, t, and Z, and their preferred embodiments, are as given above.

30 The depolymerization process is carried out at about 100°C to about 250°C, preferably about 130° to about 200°C. Although air can be used to blanket the process, it is preferred to use an inert atmosphere such as nitrogen to avoid possible side reactions. The
35 polytetrahydrofuran need not be dried before use. A

solvent may be used, but it is preferred to carry out the process without solvent.

The amount of catalyst compared to polyether present is not critical, 0.1-15% by weight being useful, preferably about 1 to 3% by weight of catalyst.

The depolymerization process may be carried out by just heating the polyether in the presence of the catalyst. In order to avoid boiling off the often volatile tetrahydrofurans, a pressure vessel may be needed. However, it is preferred to carry out the depolymerization while constantly distilling off the (substituted) tetrahydrofuran as it forms. It is believed that this ensures driving this process to produce the monomeric tetrahydrofuran. The recovered monomeric tetrahydrofuran may be used in the polymerization to form a polytetrahydrofuran.

Both the polymerization and depolymerization processes can be done in a variety of ways known to the artisan. The polymerization can be done by batch, semi-batch and continuous processes. Continuous processes include continuous stirred tank reactor(s) with one or more stages, and/or plug flow reactors (see Example 19). The depolymerization process can also be done by similar methods. In this process, a continuous process could be constant addition of polyether to the reactor, while distilling off a similar amount of a monomeric tetrahydrofuran. Other variations will be evident to one skilled in this art.

In both the polymerization and depolymerization processes disclosed herein the catalyst may be recovered and reused in either process. It may be recovered from the polymerization process by extracting the polymer formed with water, while it can be recovered from the depolymerization process by extracting the distillation residue with water. In both instances, the recovered

catalyst may be used again in the polymerization or depolymerization processes. In both instances the aqueous washings may be concentrated by removal of the water (as by evaporation) and the solid catalyst recovered. See Examples 20, and 28-32 for recovery and reuse of catalyst.

In the Examples, the following abbreviations are used:

- GPC - gel permeation chromatography
- 10 Nafion™ - a sulfonated perfluoropolymer produced by E. I. du Pont de Nemours & Co., Wilmington, DE, USA
- Mn - number average molecular weight
- Mw - weight average molecular weight
- 15 RB - round bottom
- PD - polydispersity (Mw/Mn)
- PS - polystyrene
- SS - stainless steel
- STD - standard
- 20 Tf - triflate

EXAMPLE 1

Polymerization of THF with Yttrium Triflate and Acetic Anhydride

In a dry box, yttrium triflate (0.75 g) was added to each of three separate oven dried 100 mL RB flasks equipped with stirring bars. The flasks were sealed with rubber septa and removed from the dry box and nitrogen bleeds attached. THF (20 mL) followed by acetic anhydride (0.75 mL) were added to each flask. After 15, 30 and 45 minutes, a polymerization was terminated via the addition of 5% NaOH (10 mL) and THF (50 mL). The resulting organic phases were separated and concentrated at reduced pressure and then dried under vacuum. Polymer yields and GPC analysis:

Polymer. Time	Polymer Yield (%)	Mn (PS STD)	Mw	PD
15 mins.	56.76	8180	17100	2.09
30 mins.	67.02	6630	14600	2.20
45 mins.	73.11	6210	13300	2.02

EXAMPLE 2Polymerization of THF with
Ytterbium Triflate and Acetic Anhydride

In a dry box, ytterbium triflate (0.75 g) was added
5 to each of four separate oven dried 100 mL RB flasks
equipped with stirring bars. The flasks were sealed
with rubber septa and removed from the dry box.
Nitrogen bleeds were attached and THF (20 mL) followed
by acetic anhydride (0.75 mL) were added to each flask.
10 After 15, 30, 45 and 60 minutes, a polymerization was
terminated via the addition of 5% NaOH (10 mL) and THF
(50 mL). The resulting organic phases were separated,
concentrated at reduced pressure and then dried under
vacuum. Polymer yields and GPC analysis:

Polymer. Time	Polymer Yield (%)	Mn (PS STD)	Mw	PD
15 mins.	56.09	8400	16200	1.93
30 mins.	67.98	7360	14900	2.03
45 mins.	69.67	5890	13100	2.22
60 mins.	71.31	6010	12800	2.15

15

EXAMPLE 3Polymerization of THF with
Dysprosium Triflate and Acetic Anhydride

In a dry box, dysprosium triflate (0.75 g) was
added to each of four separate oven dried 100 mL RB
20 flasks equipped with stirring bars. The flasks were
sealed with rubber septa and removed from the dry box.
After the attachment of nitrogen bleeds THF (20 mL)
followed by acetic anhydride (0.75 mL) were added to
each flask. After 15, 30, 45 and 60 minutes, a
25 polymerization was terminated via the addition of 5%

NaOH (10 mL) and THF (50 mL). The resulting organic phases were separated, concentrated at reduced pressure and then dried under vacuum. Polymer yields and GPC analysis:

Polymer. Time	Polymer Yield (%)	Mn (PS STD)	Mw	PD
15 mins.	52.03	7260	15700	2.17
30 mins.	63.86	7220	15700	2.18
45 mins.	70.05	6250	14300	2.30
60 mins.	71.36	6010	13700	2.29

5

EXAMPLE 4

Polymerization of THF with
Erbium Triflate and Acetic Anhydride

In a dry box, erbium triflate (0.75 g) was added to each of four separate oven dried 100 mL RB flasks equipped with stirring bars. After sealing with rubber septa the flasks were removed from the dry box. Nitrogen bleeds were attached and THF (20 mL) followed by acetic anhydride (0.75 mL) were added to each flask. After 15, 30, 45 and 60 minutes, a polymerization was terminated via the addition of 5% NaOH (10 mL) and THF (50 mL). The resulting organic phases were separated, concentrated at reduced pressure and then dried under vacuum. Polymer yields and GPC analysis:

Polymer. Time	Polymer Yield (%)	Mn (PS STD)	Mw	PD
15 mins.	52.82	8460	15900	1.89
30 mins.	62.96	7390	17100	2.32
45 mins.	66.79	8070	16400	2.04
60 mins.	68.20	7250	16100	2.22

EXAMPLE 5

20

Polymerization of THF with
Lanthanum Triflate and Acetic Anhydride

In a dry box, lanthanum triflate (0.75 g) was added to each of four separate oven dried 100 mL RB flasks equipped with stirring bars. The flasks were sealed

with rubber septa and then removed from the dry box. Nitrogen bleeds were attached and THF (20 mL) and acetic anhydride (0.75 mL) were added to each flask. After 15, 30, 45 and 60 minutes, a polymerization was terminated
5 via the addition of 5% NaOH (10 mL) and THF (50 mL). The resulting organic phases were separated, concentrated at reduced pressure and then dried under vacuum. Polymer yields and GPC analysis:

Polymer. Time	Polymer Yield (%)	Mn (PS STD)	Mw	PD
15 mins.	5.60	9780	13900	1.42
30 mins.	11.27	13700	20900	1.53
45 mins.	40.30	17000	28100	1.65
60 mins.	59.24	15800	33400	2.11

EXAMPLE 6

10 Polymerization of THF with Neodymium Triflate and Acetic Anhydride

In a dry box, to an oven dried 100 mL RB flask equipped with a stirring bar was added neodymium triflate (0.75 g). The flask was sealed with a rubber
15 septum and removed from the dry box. A nitrogen bleed was attached and THF (20 mL) followed by acetic anhydride (0.75 mL) were added. After 30 minutes the polymerization was terminated via the addition of 5% NaOH (10 mL) and THF (50 mL). The resulting organic
20 phase was separated, concentrated at reduced pressure and then dried under vacuum yielding 7.56 g (42.6%) of polymer. GPC analysis: Mn = 8460, Mw = 22300, PD = 2.65 (PS STD).

EXAMPLE 7

25 Polymerization of THF with Yttrium Triflate and Acetic Anhydride

In a dry box, yttrium triflate (0.75 g) was added to each of three oven dried 100 mL RB flasks equipped with stirring bars. The flasks were sealed with rubber

septa and removed from the dry box. Nitrogen bleeds were attached and THF (20 mL) added to each flask. Acetic anhydride (0.25, 0.50 and 0.75 mL) was added respectively to each flask. After 60 minutes the
5 polymerizations were quenched via the addition of 5% NaOH (10 mL) and THF (50 mL), the resulting organic phases were separated, concentrated at reduced pressure and then dried in vacuo overnight. Polymer yields and GPC analysis:

Acetic Anhydride	Polymer Yield (%)	Mn (PS STD)	Mw	PD
0.25 mL	75.02	8080	18100	2.25
0.50 mL	73.33	6940	14900	2.15
0.75 mL	75.20	5080	13600	2.68

10

EXAMPLE 8Polymerization of THF with Yttrium Triflate and Acetic Anhydride

In a dry box, to three 100 mL RB flasks equipped with stirring bar were added 0.25, 0.50 and 1.00 g
15 yttrium triflate respectively. The flask were sealed with rubber septa and removed from the dry box. Nitrogen bleeds were attached and THF (20 mL) and acetic anhydride (1.00 mL) were added to each flask. After 60 minutes the polymerizations were terminated via the
20 addition of 5% NaOH (10 mL) and THF (50 mL). The resulting organic phases were separated, concentrated at reduced pressure and dried under vacuum overnight. Polymer yields and GPC analysis:

Yttrium Triflate	Polymer Yield (%)	Mn (PS STD)	Mw	PD
0.25 g	50.11	11300	26200	2.02
0.50 g	70.79	8060	17600	2.16
1.00 g	81.96	4820	10500	2.09

EXAMPLE 9Polymerization of THF with
Yttrium Triflate and Acetic Anhydride
in Diethyl Ether

5 In a dry box, yttrium triflate (0.75 g) was weighed
into an oven dried 100 mL RB flask equipped with
stirring bar. A reflux condenser was attached and the
apparatus sealed with a rubber septum and removed from
the dry box. A nitrogen bleed was attached and diethyl
10 ether (20 mL), THF (20 mL) and acetic anhydride
(0.75 mL) were added. After 60 minutes the
polymerization was quenched via the addition of 5% NaOH
(10 mL) and diethyl ether (50 mL). The resulting
organic phase was separated, concentrated and dried
15 under vacuum. Yield: 3.86 g (21.76%). GPC analysis:
Mn = 2960, Mw = 7800, PD = 2.63 (PS STD).

EXAMPLE 10Polymerization of THF with
Yttrium Triflate and Acetic Anhydride in Toluene

20 In a dry box, yttrium triflate (0.75 g) was weighed
into an oven dried 100 mL RB flask equipped with a
stirring bar. After sealing with a rubber septum,
removal from the dry box, and attachment of a nitrogen
bleed, toluene (20 mL), THF (20 mL) and acetic anhydride
25 (0.75 mL) were added. After 60 minutes the
polymerization was terminated via the addition of 5%
NaOH (10 mL) and toluene (50 mL). The resulting organic
phase was separated, concentrated at reduced pressure
and then dried under vacuum. Yield: 1.73 g (9.75%).
30 GPC analysis: Mn = 1150, Mw = 2700, PD = 2.34 (PS STD).

EXAMPLE 11Copolymerization of THF/3-Methyl-THF
with Yttrium Triflate and Acetic Anhydride

35 In a dry box, yttrium triflate (0.75 g) was added
to each of three separate oven dried 100 mL RB flasks

equipped with stirring bars. The flasks were sealed with rubber septa and removed from the dry box wherein nitrogen bleeds were attached. THF (15 mL) and 3-methyl-THF (5 mL) followed by acetic anhydride (0.75 mL) were added to each flask. After 15, 30 and 45 minutes, a polymerization was terminated via the addition of 5% NaOH (10 mL) and THF (50 mL). The resulting organic phases were separated, concentrated at reduced pressure and then dried under vacuum. Polymer yields and GPC analysis:

Polymer. Time	Polymer Yield (%)	Mn (PS STD)	Mw	PD
15 mins.	39.50	6920	12400	1.80
30 mins.	51.63	6280	13200	2.11
45 mins.	57.27	5860	12700	2.17

¹H NMR analysis showed ~12-13% incorporation of 3-methyl-THF in the polymers.

EXAMPLE 12

Polymerization of THF with Yttrium Triflate and Trifluoroacetic Anhydride

In a dry box, yttrium triflate (0.75 g) was weighed in an oven dried 100 mL RB flask equipped with a stirring bar. After sealing with a rubber septum and removal from the dry box and attachment of a nitrogen bleed THF (20 mL) was added followed by trifluoroacetic anhydride (3.00 mL). After 2 hrs. the polymerization was quenched by the addition of 5% NaOH (10 mL) and THF (50 mL). Diethyl ether (50 mL) was added to effect separation of the organic/aqueous phase. The organic phase was separated, concentrated at reduced pressure and then dried under vacuum. Yield: 5.40 g (30.44%). GPC analysis: Mn = 53900, Mw = 86200, PD = 1.78 (PS STD).

EXAMPLE 13Polymerization of THF with
Ytterbium Triflate and Propionic Anhydride

In a dry box, ytterbium triflate (1.00 g) was
5 weighed into an oven dried 100 mL RB flask equipped with
a stirring bar. The flask was stoppered with a rubber
septum and removed from the dry box and a nitrogen bleed
was attached. THF (20 mL) and propionic anhydride
(1.00 mL) were added via syringes. After 60 minutes the
10 polymerization was quenched with 5% NaOH (10 mL) and THF
(50 mL). The resulting organic phase was separated,
concentrated at reduced pressure and then dried in
vacuo. Yield: 12.69 g (71.5%). GPC analysis:
Mn = 6520, Mw = 14500, PD = 2.23.

15 EXAMPLE 14Polymerization of 3-Methyl-THF with
Yttrium Triflate and Acetic Anhydride

In a dry box, yttrium triflate (0.75 g) was weighed
into an oven dried 100 mL RB flask equipped with a
20 stirring bar. The flask was sealed with a rubber septum
and removed from the dry box. A nitrogen bleed was
attached and 3-methyl-THF (20 mL) was added followed by
acetic anhydride (0.75 g). After stirring overnight the
polymerization was terminated by the addition of 5% NaOH
25 (10 mL) and THF (25 mL). The resulting organic phase
was separated, concentrated at reduced pressure and
dried under vacuum. Yield: 6.12 g (34.50%). GPC
analysis: Mn = 437, Mw = 808, PD = 1.85.

EXAMPLE 1530 Polymerization of THF with
Yttrium Triflate and Acetic Anhydride

In a dry box, yttrium triflate (0.75 g) was weighed
into an oven dried 100 mL RB flask equipped with a
stirring bar. After sealing with a rubber septum the
35 flask was removed from the dry box and a nitrogen bleed

attached. THF (20 mL) and acetic anhydride (1.00 mL) were added. After 17.5 hrs. THF (20 mL) and acetic anhydride (1.00 mL) were added to the thick viscous solution. After an additional 2 hrs THF (20 mL) and
5 acetic anhydride were again added to the polymerized solution. The polymerization was terminated 2.5 hrs later via the addition of 5% NaOH (20 mL) and THF (100 mL). The organic phase was separated, concentrated at reduced pressure and dried under vacuum. Polymer
10 yield: 32.3 g (61.23%). GPC analysis: $M_n = 2490$, $M_w = 8440$, $PD = 3.39$ (PS STD).

EXAMPLE 16

Polymerization of THF with Ytterbium Triflate

In a dry box, ytterbium triflate (1.00 g) was
15 weighed in a 100 mL RB flask equipped with a stirring bar. After sealing with a rubber septum the flask was removed from the dry box and a nitrogen bleed attached. THF (20 mL) was then added via syringe. The
polymerization was allowed to proceed overnight and then
20 terminated via the addition of H_2O (25 mL) and diethyl ether (75 mL). The organic phase was separated, concentrated at reduced pressure and then dried under vacuum. Polymer yield: 0.520 g (2.93%). GPC analysis:
 $M_n = 416000$, $M_w = 842000$, $PD = 2.02$ (PS STD).

EXAMPLE 17

Polymerization of 7-Oxabicyclo[2.2.1]heptane with Ytterbium Triflate and Acetic Anhydride

In a dry box, ytterbium triflate (0.5 g) was
weighed into a 100 mL RB flask equipped with a stirring
30 bar. After sealing with a rubber septum, the flask was removed from the dry box and a nitrogen bleed attached. 7-Oxabicyclo[2.2.1]heptane (10 mL, distilled from potassium carbonate) was added followed by acetic anhydride (0.5 mL). After 1 hr. the polymerization was
35 terminated by the addition of 5% NaOH (10 mL), THF

(75 mL) and diethyl ether (~50 mL). The organic phase was separate, concentrated at reduced pressure and then dried under vacuum. Polymer yield: 1.00 g. GPC analysis: $M_n = 233$, $M_w = 522$, $PD = 2.24$ (PS STD).

5

EXAMPLE 18Polymerization ofCyclohexene Oxide with Lanthanum Triflate

In a dry box, lanthanum triflate (0.75 g) was weighed in a oven dried 100 mL three neck flask equipped with a stirring bar, reflux condenser and addition funnel. Toluene (20 mL) was added via syringe and cyclohexene oxide (20 mL) was slowly added via the addition funnel. The polymerization was terminated after 2.75 hrs. via the addition of H_2O (10 mL) and toluene (100 mL). The organic phase was separated, concentrated at reduced pressure and then dried under vacuum. Polymer yield: 12.4 g (63.9%). GPC analysis (bimodal distribution): $M_n = 4510$, $M_w = 25700$, $PD = 5.70$ (PS STD).

20

EXAMPLE 19Continuous Polymerization of THF with Ytterbium Triflate and Acetic Anhydride

A solution of THF (~500 mL) and ytterbium triflate (25 g) was charged into a 500 mL capacity ISCO pump, which was connected to a 3 way 3.2 mm SS connector ("T" mixer) via 8 cm of 3.2 mm SS tubing containing a check valve. A second ISCO pump (500 mL capacity) was charged with ~100 mL of acetic anhydride and this was connected to the "T" mixer by 75 cm of 3.2 mm SS tubing also containing a check valve. The feed rate of the THF/ytterbium triflate solution was 3.3 mL/min and that of the acetic anhydride was 0.25 mL/min. The "T" mixer was connected to a glass stirred holdup tank (approximately 60 mL volume) by 12 cm of 3.2 mm SS tubing. This tank was then connected to a second

stirred holdup tank (approximately 55 mL volume) via
Cajon flex tubing with ultra torr fitting (6.4 mm,
13 cm). This in turn was connected to a third glass
reactor, plug flow (approximately 60 mL volume), again
5 via Cajon flex tubing with ultra torr fitting (6.4 mm,
13 cm). The polymerized solution exiting from the third
reactor was fed to a stirred beaker containing
water/diethyl ether. Each reactor was equipped with
thermal well port. During the polymerization the
10 temperature in the first reactor stabilized to 41-42°C
and that of the second reactor to 31-32°C and that of
the third reactor 26-27°C. After the contents of the
THF/ytterbium triflate pump was discharged, and two
fractions of polymer were collected, the pump was again
15 refilled with a solution of THF (~500 mL) and ytterbium
triflate (25 g). Three fractions were collected. The
last fraction was obtained by purging the system with
diethyl ether.

The organic phases were separated, concentrated at
20 reduced pressure and then dried under vacuum giving the
following:

Fraction	Weight
1	106.86 g
2	79.59 g
3	56.97 g
4	220.2 g
5	97.2 g

The aqueous phases from above were collected,
concentrated at reduced pressure and then dried under
vacuum at 180°C giving a cream solid, 46.98 g,
25 representing a 93.94% recovery of the total ytterbium
triflate catalyst used.

EXAMPLE 20Polymerization of THF with Ytterbium Triflate
(Recovered from Example 19) and Acetic Anhydride

In a dry box, ytterbium triflate (1.00 g),
5 recovered catalyst from Example 19, was weighed out in a
100 mL RB flask equipped with a stirring bar. A rubber
septum was attached and the flask removed from the dry
box. A nitrogen bleed was attached and THF (20 mL)
added followed by acetic anhydride (1.00 mL). After 1
10 hr. the polymerization was terminated by the addition of
water (25 mL), THF (25 mL) and diethyl ether (50 mL),
the resulting organic phase was separated, concentrated
at reduced pressure, then dried under vacuum affording
13.42 g (75.65%) of polymer.

15

EXAMPLE 21Polymerization of THF with
Yttrium Triflate and Acetic Anhydride at -78°C

In a dry box, yttrium triflate (0.75 g) was weighed
in an oven dried 100 mL RB flask equipped with a
20 stirring bar. After sealing with a rubber septum,
removal from the dry box and the attachment of a
nitrogen bleed, THF (20 mL) was added. The resulting
mixture was cooled to -78°C. Acetic anhydride (0.75 mL)
was then added, the polymerization was terminated 5 hrs.
25 later by the addition of water (25 mL) and diethyl ether
(50 mL). After warming to room temperature the
resulting organic phase was separated, concentrated at
reduced pressure, then dried under vacuum affording
0.58 g (3.27%) of polymer.

30

EXAMPLE 22Preparation of Didymium (Mischmetall) Triflate

Didymium (mischmetall) oxide (17 g) and water
(50 mL) were added to a 200 mL RB flask equipped with
stirring bar and an addition funnel and reflux
35 condenser. Triflic acid (50 g) was slowly added via the

addition funnel to the resulting stirred slurry. After the addition was completed a homogeneous solution resulted, thus an additional 2.0 g of the oxide was added and the slurry heated to reflux for 2 hrs. The cooled slurry was filtered, the filtrate concentrated at reduced pressure and then dried under vacuum at 150-210°C affording 58.4 g of a pink solid.

EXAMPLE 23

Polymerization of THF with Didymium (Mischmetall)

Triflate: Polymerization Time on Polymer Yield

In a dry box, didymium triflate (0.75 g) was added to each of four separate oven dried 100 mL RB flasks equipped with stirring bars. The flasks were sealed with rubber septa and removed from the dry box and nitrogen bleeds attached. THF (20 mL) followed by acetic anhydride (0.75 mL) were added to each flask. After 15, 30, 45 and 60 minutes, a polymerization was terminated via the addition of 5% NaOH (10 mL) and THF (50 mL). The resulting organic phases were separated, concentrated at reduced pressure and then dried under vacuum. Polymer yields:

<u>Polymer Time</u>	<u>Polymer Yield (%)</u>
15 mins.	13.92
30 mins.	34.94
45 mins.	43.74
60 mins	49.4

EXAMPLE 24

Polymerization of Refluxing THF with Yttrium Triflate and Acetic Anhydride

In a dry box, yttrium triflate (0.75 g) was weighed into an oven dried 100 mL flask equipped with a stirred bar, a reflux condenser was attached, the flask sealed with rubber septum and removed from the dry box and a nitrogen bleed attached. THF (20 mL) was added and the resulting mixture heated to reflux via an oil bath

(temp. ~80°C). Acetic anhydride (0.75 mL) was added to the stirred refluxing mixture. After 30 minutes the polymerization was terminated via the addition of 5% NaOH (10 mL) and THF (50 mL). The cooled organic phase
5 was separated, concentrated at reduced pressure, then dried under vacuum giving 6.44 g (36.30%) of polymer.

EXAMPLE 25

Preparation of Ytterbium Nafion® Salt

In a 300 mL RB flask were added ytterbium oxide
10 (0.75 g) and Nafion® perfluorinated ion exchange resin powder (300 mL, 5 wt. % solution in a mixture of lower aliphatic alcohols and 10% water). The resulting mixture was heated to 100°C and stirred overnight. The resulting solution was filtered and dried under vacuum
15 at 150°C, affording 9.21 g of a light brown solid.

EXAMPLE 26

Polymerization of THF with Ytterbium Nafion® Salt and Acetic Anhydride

In a dry box, the ytterbium Nafion® salt (1.00 g,
20 from Example 25) was added to each of four oven dried 100 mL RB flasks equipped with stirring bars. The flasks were sealed with rubber septa and removed from the dry box and nitrogen bleeds attached. THF (20 mL) followed by acetic anhydride (1.00 mL) were added to
25 each flask. After 2, 3, 4 and 5 hrs. a polymerization was terminated by the addition of water (25 mL) and diethyl ether (50 mL). The organic phases were separated, concentrated at reduced pressure and then dried under vacuum to give the following:

<u>Polymer Time</u>	<u>Polymer Yield (%)</u>
2 hrs.	5.24
3 hrs.	11.39
4 hrs.	17.08
5 hrs.	22.66

EXAMPLE 27Depolymerization of PolyTHF with Yttrium Triflate

Polytetrahydrofuran 1000 (300 g, Aldrich) and yttrium triflate (9 g) were placed in a 500 mL three neck flask equipped with a stirring bar, Vigreux column (30.5 cm) and a fractional distillation head. A nitrogen purge was then attached and all other openings glass stoppered. The resulting mixture was then heated by an oil bath and the water clear distillate fractions collected as follows:

Fraction	Oil Bath Temp (°C)	Head Temp (°C)	Weight
1	171-175	64.5	67.49
2	176	64.5	71.84
3	176	64.5	32.84
4	178	64.5	58.67
5	178	64.5	56.71

Total weight of distillate collected: 287.55

¹H NMR analyses of all five fractions confirmed the product to be THF.

Yield (Recovery): 95.85%

EXAMPLE 28Depolymerization of Poly-THF with Yttrium Triflate: Reuse of Catalyst

To the residue remaining from Example 27 was added polytetrahydrofuran 1000 (300 g, Aldrich). The apparatus was reassembled the resulting mixture heated by an oil bath, and the resulting water clear distillate fractions were collected as follows:

Fraction	Oil Bath Temp (°C)	Head Temp (°C)	Weight
1	170-174	63-64	43.39
2	174	64	62.68
3	175	65	66.15
4	177	65	55.15
5	177	65	32.58

Total weight of distillate collected: 259.95 g
Yield (Recovery): 86.65%
Total time elapsed from start of collection to termination of
Example: 2 hrs. 50 mins.

EXAMPLE 29

Polymerization of Recovered THF with Ytterbium Triflate and Acetic Anhydride

In a dry box, ytterbium triflate (1.00 g) was added
5 to an oven dried 100 mL flask equipped with a stirring
bar. The flask was then sealed with a rubber septum and
removed from the dry box and a nitrogen purge attached.
Tetrahydrofuran (20 mL) from the fourth fraction of
Example 27 was added followed by 1 mL of acetic
10 anhydride. After 1 hour no polymerization was apparent,
thus an additional 1 mL of acetic anhydride added.
After 1 hour the polymerization was terminated via the
addition of 5% NaOH and THF (50 mL), the organic phase
separated, concentrated at reduced pressure and then
15 dried in vacuo overnight affording 10.31 g (58%) of
polymer. GPC analysis: $M_n = 1970$, $M_w = 6650$, $PD = 3.38$
(PS STD).

EXAMPLE 30

Polymerization of Recovered Purified THF 20 with Ytterbium Triflate and Acetic Anhydride

Fractions 2-4 of experiment Example 27 were
combined and distilled from sodium/benzophenone. Twenty
mL of this dried THF was added to ytterbium triflate (1
g), previously weighed out in an oven dried 100 mL flask
25 equipped with stirring bar and a nitrogen purge. Acetic
anhydride (1 mL) was then added, after 1 hour the
polymerization was terminated via the addition of 5%
NaOH and THF (50 mL), the organic phase separated and
concentrated at reduced pressure and then in vacuo,
30 affording 13.32 g (78.08%) of polymer. GPC analysis:
 $M_n = 4110$, $M_w = 8860$, $PD = 2.15$ (PS STD).

EXAMPLE 31Recovery of Catalyst from Depolymerization

Water (100 mL) was added to the residue from Example 28; the resulting mixture was stirred at room temperature for approximately 1 hour, the aqueous phase separated and concentrated at reduced pressure and dried in vacuo at 180°C overnight affording a brown solid. This solid was again dissolved in water, then filtrated, the filtrated concentrated at reduced pressure. The resulting solid was dried under vacuum at 180°C overnight affording a cream solid: 6.48 g (72%) of recovered catalyst.

EXAMPLE 32Activity of Recovered Catalyst
in the Polymerization of THF

In a dry box, the recovered catalyst of Example 31 (1 g) was placed in an oven dried 100 mL flask equipped with a stirring bar. The flask was sealed with a rubber septum and removed from the dry box and a nitrogen purge attached. THF (20 mL) was then added followed by acetic anhydride (1 mL). After 1 hour the polymerization was terminated via the the addition of 5% NaOH and THF (50 mL), the organic phase separated, concentrated and dried in vacuo overnight affording 13.86 g (78.13%) of polymer. GPC Analysis: Mn = 4460, Mw = 9280, PD = 2.08 (PS STD).

EXAMPLE 33Depolymerization of Poly-THF/3-Methyl-THF
Copolymer with Yttrium Triflate

Poly-tetrahydrofuran/3-methyl-tetrahydrofuran copolymer (308.6 g) containing 3385 ppm water and yttrium triflate (9 g) were placed in a 500 mL three neck flask equipped with a stirring bar, Vigreux column (30.5 cm), a thermometer and a fractional distillation head. A nitrogen purge was attached and all other

opening glass stoppered. The resulting mixture was heated by an oil bath and the water clear distillate fractions collected as follows:

Fraction	Oil Bath Temp. (°C)	Rxn. Temp. (°C)	Head Temp. (°C)	Weight (g)
1	180-182	140-145	65-70	64.35
2	182-184	140	69-70	71.03
3	183-185	140-144	70	69.35
4	185	143	70	70.12
5	185	-	70	22.35

Total Weight Collected: 297.20 g

% Yield (Recovery): 96.47

Total depolymerization time: 2 hrs. 25 mins.

EXAMPLE 34

5

Depolymerization of PolyTHF.

Diacetate Capped, with Yttrium Triflate

Polytetrahydrofuran which was diacetate capped (300 g, Mn 1850) and yttrium triflate (9 g) were placed in a 500 mL three flask equipped with a stirring bar, Vigreux (30.5 cm), a thermometer and a fractional distillation head. A nitrogen purge was attached and all other openings glass stoppered. The resulting mixture was heated by an oil bath and the water clear distillate fractions collected as follows:

Fraction	Oil Bath Temp. (°C)	Rxn. Temp. (°C)	Head Temp. (°C)	Weight (g)
1	158-160	105-129	64	82.78
2	160-161	116-129	64-66	62.91
3	161	116	64-67	77.71
4	161-180	-	67-69	51.50

Total weight Collected: 274.90 g

% Yield (Recovery): 91.63

Total depolymerization time: 1 hr. 25 mins.

10

EXAMPLE 35Polymerization of THF with Bis(*n*-cyclopentadienyl)-
tetrahydrofuran-bis(trifluoromethanesulfonato)-
zirconium and Acetic Anhydride

- 5 In a dry box, bis(*n*-cyclopentadienyl)tetrahydro-
furan-bis(trifluoromethanesulfonato)zirconium (0.50 g)
was added to each of four separate oven dried 100 mL RB
flasks equipped with stirring bars. The flasks were
sealed with rubber septa and removed from the dry box.
- 10 After the attachment of nitrogen bleeds THF (10 mL) and
acetic anhydride (0.50 mL) were added to each flask.
After 15, 30, 45 and 60 minutes, a polymerization was
terminated via the addition of water (25 mL), THF
(50 mL) and ether (25 mL). The resulting organic phases
- 15 were separated, concentrated at reduced pressure and
then dried under vacuum. Polymer yields and GPC
analysis:

Polymer. Time	Polymer Yield (%)	Mn (PS STD)	Mw	PD
15 mins.	39.34	12700	14100	1.11
30 mins.	54.79	15000	19000	1.27
45 mins.	63.92	16000	22100	1.38
60 mins.	64.26	17200	24500	1.41

EXAMPLE 36Polymerization of THF with Bis(*n*-cyclopentadienyl)-
20 bis(trifluoromethanesulfonato)titanium
and Acetic Anhydride

- In a dry box, bis(*n*-cyclopentadienyl)-bis(tri-
fluoromethanesulfonato)titanium (0.50 g) was added to
each of four separate oven dried 100 mL RB flasks
- 25 equipped with stirring bars. The flasks were sealed
with rubber septa and then removed from the dry box.
Nitrogen bleeds were attached and THF (10 mL) and acetic
anhydride (0.50 mL) were added to each flask. After 15,
30, 45, 70 minutes a polymerization was terminated via

the addition of water (25 mL), ether (25 mL) and THF (50 mL). The separated organic phases were washed repeatedly with water (3 x 25 mL), then separated, concentrated at reduced pressure and then dried under vacuum. Polymer yields and GPC analysis:

Polymer. Time	Polymer Yield (%)	Mn (PS STD)	Mw	PD
15 mins.	39.35	10700	12000	1.12
30 mins.	61.33	13900	17300	1.25
45 mins.	67.08	14200	19300	1.35
70 mins.	65.50	12400	19300	1.56

EXAMPLE 37

Polymerization of THF with Bis(*n*-cyclopentadienyl)tetrahydrofuran-bis(trifluoromethanesulfonato)zirconium and Acetyl Chloride

10 In a dry box, bis(*n*-cyclopentadienyl)tetrahydrofuran-bis(trifluoromethanesulfonato)zirconium (0.50 g) was added to each of three separate oven dried 100 mL RB flasks equipped with stirring bars. The flasks were sealed with rubber septa and removed from the dry box.

15 After the attachment of nitrogen bleeds, THF (10 mL) and acetyl chloride (0.375 mL) were added to each flask. After 15, 30, and 45 minutes, a polymerization was terminated via the addition of water (25 mL), THF (50 mL) and ether (25 mL). The resulting organic phases

20 were washed repeatedly with water (3 x 25 mL), separated, concentrated at reduced pressure and then dried under vacuum. Polymer yields and GPC analysis:

Polymer. Time	Polymer Yield (%)	Mn (PS STD)	Mw	PD
15 mins.	59.86	7980	10800	1.35
30 mins.	68.88	7470	11000	1.48
45 mins.	68.65	5620	9920	1.76

EXAMPLE 38Polymerization of THF with Bis(*n*-cyclopentadienyl)-
bis(trifluoromethanesulfonato)titanium
and Acetyl Chloride

- 5 In a dry box, bis(*n*-cyclopentadienyl)-bis(tri-
fluoromethanesulfonato)titanium (0.50 g) was added to
each of three separate oven dried 100 mL RB flasks
equipped with stirring bars. The flasks were sealed
with rubber septa and then removed from the dry box.
- 10 Nitrogen bleeds were attached and THF (10 mL) and acetyl
chloride (0.375 mL) were added to each flask. After 15,
30, and 45 minutes a polymerization was terminated via
the addition of water (25 mL), ether (25 mL) and THF
(50 mL). The separated organic phases were washed
- 15 repeatedly with water (3 x 25 mL), then separated,
concentrated at reduced pressure and then dried under
vacuum. Polymer yields:

<u>Polymer. Time</u>	<u>Polymer Yield (%)</u>
15 mins.	46.11
30 mins.	66.85
45 mins.	74.97

EXAMPLE 39

- 20 Polymerization of THF with Bis(*n*-cyclopenta-
dienyl)tetrahydrofuran-bis(trifluoromethane-
sulfonato)zirconium and Acetic Anhydride

- In a dry box, bis(*n*-cyclopentadienyl)tetrahydro-
furan-bis(trifluoromethanesulfonato)zirconium (0.50 g)
was added to each of three separate oven dried 100 mL RB
- 25 flasks equipped with stirring bars. The flasks were
sealed with rubber septa and removed from the dry box.
After the attachment of nitrogen bleeds THF (20 mL) and
acetic anhydride (1.00 mL) were added to each flask.
After 15, 30, and 45 minutes, a polymerization was
- 30 terminated via the addition of water (25 mL), THF
(50 mL) and ether (25 mL). The resulting organic phases

were separated, concentrated at reduced pressure and then dried under vacuum. Polymer yields and GPC analysis:

Polymer. Time	Polymer Yield (%)	Mn (PS STD)	Mw	PD
15 mins.	15.22	11300	11900	1.05
30 mins.	30.50	18100	20300	1.12
45 mins.	39.35	21300	25500	1.20

EXAMPLE 40

5 Copolymerization of THF and 3-Methyl-THF with
 Bis(n-cyclopentadienyl)tetrahydrofuran-
 bis(trifluoromethanesulfonato)zirconium
 and Acetic Anhydride

10 In a dry box, bis(n-cyclopentadienyl)tetrahydro-
furan-bis(trifluoromethanesulfonato)zirconium (0.50 g)
was added to each of three separate oven dried 100 mL RB
flasks equipped with stirring bars. The flasks were
sealed with rubber septa and removed from the dry box.
After the attachment of nitrogen bleeds THF (7.5 mL),
15 3-Methyl-THF (2.5 mL) and acetic anhydride (0.10 mL)
were added to each flask. After 15, 30, and 45 minutes,
a polymerization was terminated via the addition of
water (25 mL), THF (50 mL) and ether (25 mL). The
resulting organic phases were separated, concentrated at
20 reduced pressure and then dried under vacuum. ¹H NMR
analysis indicates ~10.5% incorporation of 3-methyl-THF
in the polymers. Polymer yields and GPC analysis:

Polymer. Time	Polymer Yield (%)	Mn (PS STD)	Mw	PD
15 mins.	24.8	8500	9430	1.11
30 mins.	41.15	11400	13300	1.17
45 mins.	49.15	12200	15500	1.27

EXAMPLE 41Preparation of Bis(*n*-cyclopentadienyl)tetra-
hydrofuran-bis(trifluoromethanesulfonato)hafnium

In a dry box, hafnocene dichloride (9.93 g) was
5 dissolved in THF (300 mL). To this solution, with
stirring, was added a solution of silver triflate
(14.12 g) in THF (100 mL). After 10 minutes the
precipitated silver chloride was filtered off and the
resulting filtrate concentrated to approximately half
10 its volume at reduced pressure. Hexane (250 mL) was
added and the resulting mixture placed in the freezer.
The resulting precipitate was filtered and then dried
under vacuum. Yield: 10.02 g. ^1H NMR (CDCl_3): 6.68
(s, 10 H), 3.76 (m, 4H), 1.84 (m, 4H).

EXAMPLE 42Preparation of Bis(pentamethyl-*n*-cyclopentadienyl)-
bis(trifluoromethanesulfonato)zirconium

In a dry box, bis(pentamethylcyclopentadienyl)-
zirconium dichloride (10.00 g) was dissolved in THF
20 (300 mL). To this solution, with stirring, was added a
solution of silver triflate (12.46 g) in THF (100 mL).
After 15 minutes the precipitated silver chloride was
filtered off and the resulting filtrate concentrated to
approximately half its volume at reduced pressure.
25 Hexane (250 mL) was added and the resulting mixture
placed in the freezer. The resulting yellow precipitate
was filtered and then dried under vacuum. Yield:
6.02 g. ^1H NMR (CDCl_3): 2.12 (s).

EXAMPLE 43Preparation of Bis(*n*-cyclopentadienyl)-
bis(trifluoromethanesulfonato)vanadium

In a dry box, vanadocene dichloride (5.00 g) was
dissolved in THF (300 mL). To this solution, with
stirring, was added a solution of silver triflate
35 (11.19 g) in THF (100 mL). After 15 minutes the

- precipitated silver chloride was filtered off and the resulting filtrate concentrated to approximately half its volume at reduced pressure. Hexane (250 mL) was added and the resulting mixture placed in the freezer.
- 5 The resulting green precipitate was filtered and then dried under vacuum. Yield: 6.99 g.

EXAMPLE 44

10 Polymerization of THF with bis(n-cyclopentadienyl)tetrahydrofuranbis(trifluoromethanesulfonato)-zirconium and Acetic Anhydride in Hexane

- In a dry box, bis(n-cyclopentadienyl)tetrahydrofuran-bis(trifluoromethanesulfonato)zirconium (0.50 g) was added to each of three separate oven dried 100 mL RB flasks equipped with stirring bars. The flasks were
- 15 sealed with rubber septa and removed from the dry box. After the attachment of nitrogen bleeds hexane (10 mL), THF (20 mL) and acetic anhydride (0.10 mL) were added to each flask. After 15, 30, and 45 minutes, a polymerization was terminated via the addition of water
- 20 (25 mL), THF (50 mL) and ether (25 mL). The resulting organic phases were separated, concentrated at reduced pressure and then dried under vacuum. Polymer yields and GPC analysis:

Polymer. Time	Polymer Yield (%)	Mn (PS STD)	Mw	PD
15 mins.	4.96	1390	2020	1.45
30 mins.	9.24	2980	3470	1.16
45 mins.	20.40	3410	4030	1.18

EXAMPLE 45

25 Polymerization of Cyclohexene Oxide with bis(n-cyclopentadienyl)tetrahydrofuran-bis(trifluoromethanesulfonato)zirconium

- In a dry box, bis(n-cyclopentadienyl)tetrahydrofuran-bis(trifluoromethanesulfonato)zirconium (0.50 g)
- 30 was added to an oven dried 100 mL RB flask equipped with

stirring bar, reflux condenser and addition funnel. The flask was sealed with a rubber septum and removed from the dry box. After the attachment of a nitrogen bleed, toluene (10 mL) was added. Then a solution of

5 cyclohexene oxide (20 mL) and toluene (10 mL) was slowly added via the addition funnel. After 60 minutes the polymerization was terminated by the addition of water (25 mL) and toluene (100 mL). The separated organic phase was concentrated at reduced pressure and then

10 dried under vacuum. Polymer yield: 2.28 g. GPC analysis (PS STD.): Mn = 13600, Mw = 24500, PD = 1.80.

EXAMPLE 46

Polymerization of THF with
Bis(*n*-cyclopentadienyl)tetrahydrofuran-
15 bis(trifluoromethanesulfonato)hafnium
and Acetic Anhydride

In a dry box, bis(*n*-cyclopentadienyl)tetrahydrofuran-bis(trifluoromethanesulfonato)hafnium (0.50 g) was added to each of four separate oven dried 100 mL RB

20 flasks equipped with stirring bars. The flasks were sealed with rubber septa and removed from the dry box. After the attachment of nitrogen bleeds THF (10 mL) and acetic anhydride (0.50 mL) were added to each flask. After 15, 30, 45 and 60 minutes, a polymerization was

25 terminated via the addition of water (25 mL), THF (50 mL) and ether (25 mL). The resulting organic phases were separated, concentrated at reduced pressure and then dried under vacuum. Polymer yields and GPC analysis:

Polymer. Time	Polymer Yield (%)	Mn (PS STD)	Mw	PD
15 mins.	32.13	11200	12200	1.09
30 mins.	48.70	15200	18600	1.22
45 mins.	58.74	17400	23100	1.33
60 mins.	60.54	17000	24100	1.42

EXAMPLE 47Polymerization of THF with Bis(n-cyclopentadienyl)-
bis(trifluoromethanesulfonato)vanadium
and Acetic Anhydride

5 In a dry box, bis(n-cyclopentadienyl)-bis(tri-
fluoromethanesulfonato)vanadium (0.50 g) was added to
each of four separate oven dried 100 mL RB flasks
equipped with stirring bars. The flasks were sealed
with rubber septa and removed from the dry box. After
10 the attachment of nitrogen bleeds THF (10 mL) and
acetic anhydride (0.50 mL) were added to each flask.
After 15, 30, 45 and 60 minutes, a polymerization was
terminated via the addition of water (25 mL), THF
(50 mL) and ether (25 mL). The resulting organic phases
15 were separated, concentrated at reduced pressure and
then dried under vacuum. Polymer yields and GPC
analysis:

Polymer. Time	Polymer Yield (%)	Mn (PS STD)	Mw	PD
15 mins.	17.59	10600	13000	1.22
30 mins.	45.32	14100	18800	1.34
45 mins.	60.43	15100	21700	1.44
60 mins.	62.57	10500	21000	2.00

EXAMPLE 48

20 Polymerization of THF with Bis(pentamethyl-
cyclopentadienyl)bis(trifluoromethanesulfonato)-
zirconium and Acetic Anhydride

 In a dry box, bis(pentamethylcyclopentadienyl)-
bis(trifluoromethanesulfonato)zirconium (0.50 g) was
added to each of four separate oven dried 100 mL RB
25 flasks equipped with stirring bars. The flasks were
sealed with rubber septa and removed from the dry box.
After the attachment of nitrogen bleeds THF (10 mL) and
acetic anhydride (0.50 mL) were added to each flask.
After 15, 30, 45 and 60 minutes, a polymerization was

terminated via the addition of water (25 mL), THF (50 mL) and ether (25 mL). The resulting organic phases were separated, concentrated at reduced pressure and then dried under vacuum. Polymer yields and GPC

5 analysis:

Polymer. Time	Polymer Yield (%)	Mn (PS STD)	Mw	PD
15 mins.	33.26	10600	11900	1.12
30 mins.	44.64	12100	14800	1.23
45 mins.	60.09	13400	17600	1.31
60 mins.	70.23	15100	20900	1.38

EXAMPLE 49

Polymerization of THF with Bis(pentamethyl-
cyclopentadienyl)bis(trifluoromethanesulfonato)-
zirconium and Adipoyl Chloride

10 In a dry box, bis(pentamethylcyclopentadienyl)-
bis(trifluoromethanesulfonato)zirconium (0.50 g) was
added to an oven dried 100 mL RB flask equipped with a
stirring bar. The flask was sealed with a rubber septum
and removed from the dry box. After the attachment of a
15 nitrogen bleed THF (10 mL) and adipoyl chloride
(0.50 mL) were added. After 45 minutes, the
polymerization was terminated via the addition of water
(25 mL), THF (50 mL) and ether (25 mL). The resulting
organic phase was separated, concentrated at reduced
20 pressure and then dried under vacuum. Polymer yield:
5.87 g (66.17%).

EXAMPLE 50

Polymerization of THF with
Bis(pentamethylcyclopentadienyl)-
25 bis(trifluoromethanesulfonato)-
zirconium and Acetyl Bromide

In a dry box, bis(pentamethylcyclopentadienyl)-
bis(trifluoromethanesulfonato)zirconium (0.50 g) was
added to an oven dried 100 mL RB flask equipped with a

stirring bar. The flask was sealed with rubber septum and removed from the dry box. After the attachment of a nitrogen bleed THF (10 mL) and acetyl bromide (0.50 mL) were added. After 45 minutes, the polymerization was
5 terminated via the addition of water (25 mL), THF (50 mL) and ether (25 mL). The resulting organic phase was separated, concentrated at reduced pressure and then dried under vacuum. Polymer yield: 2.20 g.

EXAMPLE 51

10 Polymerization of THF with Bis(n-cyclopentadienyl)-
bis(trifluoromethanesulfonato)vanadium
and Acetyl Bromide

In a dry box, bis(n-cyclopentadienyl)-bis(tri-
fluoromethanesulfonato)vanadium (0.50 g) was added to an
15 oven dried 100 mL RB flask equipped with a stirring bar. The flask was sealed with rubber septum and removed from the dry box. After the attachment of a nitrogen bleed THF (10 mL) and acetyl bromide (0.50 mL) were added. After 60 minutes, the polymerization was terminated via
20 the addition of water (25 mL), THF (50 mL) and ether (25 mL). The resulting organic phase was separated, concentrated at reduced pressure and then dried under vacuum. Polymer yield: 3.68 g.

EXAMPLE 52

25 Polymerization of THF with Bis(n-cyclopenta-
dienyl)tetrahydrofuran-bis(trifluoromethane-
sulfonato)hafnium and Acetyl Bromide

In a dry box, bis(n-cyclopentadienyl)tetrahydro-
furan-bis(trifluoromethanesulfonato)hafnium (0.50 g) was
30 added to an oven dried 100 mL RB flask equipped with a stirring bar. The flask was sealed with a rubber septum and removed from the dry box. After the attachment of a nitrogen bleed THF (10 mL) and acetyl bromide (0.50 mL) were added. After 30 minutes, the polymerization was
35 terminated via the addition of water (25 mL), THF

(50 mL) and ether (25 mL). The resulting organic phase was separated, concentrated at reduced pressure and then dried under vacuum. Polymer yield: 2.29 g.

EXAMPLE 53

5 Polymerization of Oxepane with bis(n-cyclopentadienyl)tetrahydrofuran-bis(trifluoromethanesulfonato)zirconium and Acetic anhydride

In a dry box, bis(n-cyclopentadienyl)tetrahydrofuran-bis(trifluoromethanesulfonato)zirconium (0.05 g)
10 was added to an oven dried 50 mL RB flask equipped with stirring bar. The flask was sealed with a rubber septum and removed from the dry box. After the attachment of a nitrogen bleed oxepane (1.00 mL) and acetic
anhydride. (0.05 mL) were added via syringe. After 60
15 minutes the polymerization was terminated by the addition of water (10 mL) and ether (25 mL). The separated organic phase was concentrated at reduced pressure and then dried under vacuum. Polymer yield:
0.87 g.

20

EXAMPLE 54

Polymerization of THF with Bis(n-cyclopentadienyl)tetrahydrofuran-bis(trifluoromethanesulfonato)zirconium and Diglycolyl Chloride

In a dry box, bis(n-cyclopentadienyl)tetrahydrofuran-bis(trifluoromethane-sulfonato)zirconium (0.50 g)
25 was added an oven dried 100 mL RB flask equipped with a stirring bar. The flask was sealed with a rubber septum and removed from the dry box. After the attachment of a nitrogen bleed THF (10 mL) and diglycolyl chloride
30 (1.00 mL) were added to the flask. After 45 minutes the polymerization was terminated via the addition of water (25 mL), THF (50 mL) and ether (25 mL). The resulting organic phase was separated, concentrated at reduced pressure and then dried under vacuum. Polymer yield:
35 0.64 g.

EXAMPLE 55Copolymerization of THF/3-Methyl-THF with
Bis(n-cyclopentadienyl)tetrahydrofuran-
bis(trifluoromethanesulfonato)zirconium
and Diglycolyl Chloride

5 In a dry box, bis(n-cyclopentadienyl)tetrahydro-
furan-bis(trifluoromethanesulfonato)zirconium (0.50 g)
was added an oven dried 100 mL RB flask equipped with a
stirring bar. The flask was sealed with a rubber septum
10 and removed from the dry box. After the attachment of a
nitrogen bleed THF (7.5 mL), 3-methyl-THF (2.5 mL) and
diglycolyl chloride (1.00 mL) were added to the flask.
After 45 minutes the polymerization was terminated via
the addition of water (25 mL), THF (50 mL) and ether
15 (25 mL). The resulting organic phase was separated,
concentrated at reduced pressure and then dried under
vacuum. Polymer yield: 0.63 g.

EXAMPLE 56

20 Polymerization of THF with Bis(penta-
methylcyclopentadienyl)-bis(trifluoro-
methanesulfonato)zirconium and
Trifluoroacetic Anhydride

In a dry box, bis(pentamethylcyclopentadienyl)-
bis(trifluoromethanesulfonato)zirconium (0.50 g) was
25 added to an oven dried 100 mL RB flask equipped with a
stirring bar. The flask was sealed with a rubber septum
and removed from the dry box. After the attachment of a
nitrogen bleed THF (10 mL) and trifluoroacetic anhydride
(0.50 mL) were added. After 3 hrs., the polymerization
30 was terminated via the addition of water (25 mL), THF
(50 mL) and ether (25 mL). The resulting organic phase
was separated, concentrated at reduced pressure and then
dried under vacuum. Polymer yield: 4.89 g.

EXAMPLE 57Copolymerization of THF/3-Methyl-THF with
Bis(n-cyclopentadienyl)tetrahydrofuran-
bis(trifluoromethanesulfonato)zirconium
5 and Adipoyl Chloride

In a dry box, bis(n-cyclopentadienyl)tetrahydro-
furan-bis(trifluoromethanesulfonato)zirconium (0.50 g)
was added an oven dried 100 mL RB flask equipped with a
stirring bar. The flask was sealed with a rubber septum
10 and removed from the dry box. After the attachment of a
nitrogen bleed THF (7.5 mL), 3-methyl-THF (2.5 mL) and
adipoyl chloride (1.00 mL) were added to the flask.
After 60 minutes the polymerization was terminated via
the addition of water (25 mL), THF (50 mL) and ether
15 (25 mL). The resulting organic phase was separated,
concentrated at reduced pressure and then dried under
vacuum. Polymer yield: 5.98 g.

EXAMPLE 58Polymerization of THF with Yttrium
20 Triflate and Acetyl Chloride

In a dry box, yttrium triflate (0.75 g) was added
to each of four separate oven dried 100 mL RB flasks
equipped with stirring bars. The flasks were sealed
with rubber septa and then removed from the dry box.
25 Nitrogen bleeds were attached and THF (20 mL) and acetyl
chloride (0.75 mL) were added to each flask. After 15,
30, 45 and 60 minutes a polymerization was terminated
via the addition of water (25 mL), ether (25 mL) and THF
(50 mL). The resulting organic phases were separated,
30 concentrated at reduced pressure and then dried under
vacuum. Polymer yields and GPC analysis:

Polymer. Time	Polymer Yield (%)	Mn (PS STD)	Mw	PD
15 mins.	49.21	1610	3470	2.15
30 mins.	50.05	1520	3390	2.22
45 mins.	49.77	1510	3570	2.36
60 mins.	52.76	1740	3940	2.26

EXAMPLE 59Polymerization of THF with Ytterbium
Triflate and Acetyl Chloride

In a dry box, ytterbium triflate (0.75 g) was added
5 to each of three separate oven dried 100 mL RB flasks
equipped with stirring bars. The flasks were sealed
with rubber septa and then removed from the dry box.
Nitrogen bleeds were attached and THF (20 mL) and acetyl
chloride (0.75 mL) were added to each flask. After 15,
10 30 and 45 minutes a polymerization was terminated via
the addition of water (25 mL), ether (25 mL) and THF
(50 mL). The resulting organic phases were separated,
concentrated at reduced pressure and then dried under
vacuum. Polymer yields and GPC analysis:

Polymer. Time	Polymer Yield (%)	Mn (PS STD)	Mw	PD
15 mins.	52.59	1710	3790	2.22
30 mins.	52.82	1730	4540	2.61
45 mins.	52.25	1730	4690	2.71

15 EXAMPLE 60Polymerization of THF with Didymium (Mischmetall)
Triflate and Acetyl Chloride

In a dry box, didymium triflate (0.75 g) was added
to each of three separate oven dried 100 mL RB flasks
20 equipped with stirring bars. The flasks were sealed
with rubber septa and then removed from the dry box.
Nitrogen bleeds were attached and THF (20 mL) and acetyl
chloride (0.75 mL) were added to each flask. After 15,
30 and 45 minutes a polymerization was terminated via
25 the addition of water (25 mL), ether (25 mL) and THF

(50 mL). The resulting organic phases were separated, concentrated at reduced pressure and then dried under vacuum. Polymer yields and GPC analysis:

Polymer. Time	Polymer Yield (%)	Mn (PS STD)	Mw	PD
15 mins.	21.98	1020	2000	1.95
30 mins.	26.94	926	1780	1.92
45 mins.	32.86	1040	2060	1.97

EXAMPLE 61

5 Polymerization of THF with Erbium Triflate and Acetyl Chloride

In a dry box, erbium triflate (0.75 g) was added to each of three separate oven dried 100 mL RB flasks equipped with stirring bars. The flasks were sealed with rubber septa and then removed from the dry box. Nitrogen bleeds were attached and THF (20 mL) and acetyl chloride (0.75 mL) were added to each flask. After 15, 30 and 45 minutes a polymerization was terminated via the addition of water (25 mL), ether (25 mL) and THF (50 mL). The resulting organic phases were separated, concentrated at reduced pressure and then dried under vacuum. Polymer yields and GPC analysis:

Polymer. Time	Polymer Yield (%)	Mn (PS STD)	Mw	PD
15 mins.	53.83	1570	3400	2.17
30 mins.	56.09	1650	4090	2.47
45 mins.	56.99	1710	4310	2.51

EXAMPLE 62

20 Polymerization of THF with Scandium Triflate and Acetyl Chloride

In a dry box, scandium triflate (0.75 g) was added to each of three separate oven dried 100 mL RB flasks equipped with stirring bars. The flasks were sealed with rubber septa and then removed from the dry box. Nitrogen bleeds were attached and THF (20 mL) and acetyl chloride (0.75 mL) were added to each flask. After 15,

30 and 45 minutes a polymerization was terminated via the addition of water (25 mL), ether (25 mL) and THF (50 mL). The resulting organic phases were separated, concentrated at reduced pressure and then dried under vacuum. Polymer yields and GPC analysis:

Polymer. Time	Polymer Yield (%)	Mn (PS STD)	Mw	PD
15 mins.	53.33	1750	4180	2.38
30 mins.	54.17	1690	4630	2.73
45 mins.	53.49	1570	5660	3.61

EXAMPLE 63

Polymerization of THF with Copper Triflate and Acetyl Chloride

In a dry box, copper triflate (0.75 g) was added to each of three separate oven dried 100 mL RB flasks equipped with stirring bars. The flasks were sealed with rubber septa and then removed from the dry box. Nitrogen bleeds were attached and THF (20 mL) and acetyl chloride (0.75 mL) were added to each flask. After 15, 30 and 45 minutes a polymerization was terminated via the addition of water (25 mL), ether (25 mL) and THF (50 mL). The resulting organic phases were separated, concentrated at reduced pressure and then dried under vacuum. Polymer yields and GPC analysis:

Polymer. Time	Polymer Yield (%)	Mn (PS STD)	Mw	PD
15 mins.	23.56	1010	2150	2.13
30 mins.	31.74	1250	2720	2.18
45 mins.	43.24	1390	3180	2.29

EXAMPLE 64

Polymerization of THF with Tin Triflate and Acetyl Chloride

In a dry box, tin triflate (0.75 g) was added to each of three separate oven dried 100 mL RB flasks equipped with stirring bars. The flasks were sealed with rubber septa and then removed from the dry box.

Nitrogen bleeds were attached and THF (20 mL) and acetyl chloride (0.75 mL) were added to each flask. After 15, 30 and 45 minutes a polymerization was terminated via the addition of water (25 mL), ether (25 mL) and THF (50 mL). The resulting organic phases were separated, concentrated at reduced pressure and then dried under vacuum. Polymer yields:

Polymer. Time	Polymer Yield (%)
15 mins.	23.96
30 mins.	40.53
45 mins.	41.60

EXAMPLE 65

Polymerization of THF with Zirconium

Triflate and Acetyl Chloride

In a dry box, zirconium triflate (0.75 g) was added to each of three separate oven dried 100 mL RB flasks equipped with stirring bars. The flasks were sealed with rubber septa and then removed from the dry box. Nitrogen bleeds were attached and THF (20 mL) and acetyl chloride (0.75 mL) were added to each flask. After 15, 30 and 45 minutes a polymerization was terminated via the addition of water (25 mL), ether (25 mL) and THF (50 mL). The resulting organic phases were separated, concentrated at reduced pressure and then dried under vacuum. Polymer yields and GPC analysis:

Polymer. Time	Polymer Yield (%)	Mn (PS STD)	Mw	PD
15 mins.	49.04	2040	4320	2.12
30 mins.	64.43	2200	4880	2.21
45 mins.	65.84	2290	5190	2.27

EXAMPLE 66

Polymerization of THF with Zinc Triflate and Acetyl Chloride

In a dry box, zinc triflate (0.75 g) was added to each of three separate oven dried 100 mL RB flasks

equipped with stirring bars. The flasks were sealed with rubber septa and then removed from the dry box. Nitrogen bleeds were attached and THF (20 mL) and acetyl chloride (0.75 mL) were added to each flask. After 45, 5 60 and 75 minutes a polymerization was terminated via the addition of water (25 mL), ether (25 mL) and THF (50 mL). The resulting organic phases were separated, concentrated at reduced pressure and then dried under vacuum. Polymer yields:

Polymer. Time	Polymer Yield (%)
15 mins.	5.64
30 mins.	6.88
45 mins.	7.61

10

EXAMPLE 67Polymerization of THF with Yttrium
Triflate and Adipoyl Chloride

In a dry box, yttrium triflate (1.00 g) was added to each of three separate oven dried 100 mL RB flasks 15 equipped with stirring bars. The flasks were sealed with rubber septa and then removed from the dry box. Nitrogen bleeds were attached and THF (20 mL) and adipoyl chloride (1.00 mL) were added to each flask. After 15, 30 and 45 minutes a polymerization was 20 terminated via the addition of water (25 mL), ether (25 mL) and THF (50 mL). The resulting organic phases were separated, concentrated at reduced pressure and then dried under vacuum. Polymer yields and GPC analysis:

Polymer. Time	Polymer Yield (%)	Mn (PS STD)	Mw	PD
15 mins.	56.20	2020	4350	2.16
30 mins.	58.62	2350	4790	2.04
45 mins.	58.40	1910	5250	2.75

EXAMPLE 68Polymerization of THF with Terephthaloyl
Chloride and Yttrium Triflate

In a dry box, yttrium triflate (0.75 g) and
5 terephthaloyl chloride (2.00 g) were added to a 100 mL
RB flask equipped with a stirring bar. The flask was
sealed with a rubber septum and removed from the dry
box. A nitrogen purge was attached and THF (20 mL)
added via syringe. After 90 minutes the
10 polymerization was terminated by the addition of water
(25 mL) and THF (25 mL) and ether (50 mL). The
separated organic phase was concentrated at reduced
pressure and then dried under vacuum. Polymer yield:
2.25 g. GPC Analysis (PS STD.): $M_n = 40900$,
15 $M_w = 63000$, $PD = 1.54$.

EXAMPLE 69Polymerization of THF with Neodymium
Triflate and Acetyl Bromide

In a dry box, neodymium triflate (0.75 g) was added
20 to each of four separate oven dried 100 mL RB flasks
equipped with stirring bars. The flasks were sealed
with rubber septa and then removed from the dry box.
Nitrogen bleeds were attached and THF (20 mL) and acetyl
bromide (1.50 mL) were added to each flask. After 15,
25 30, 45 and 60 minutes a polymerization was terminated
via the addition of water (25 mL), ether (25 mL) and THF
(50 mL). The resulting organic phases were separated,
concentrated at reduced pressure and then dried under
vacuum. Polymer yields:

<u>Polymer. Time</u>	<u>Polymer Yield (%)</u>
15 mins.	27.11
30 mins.	27.06
45 mins.	28.13
60 mins.	27.28

EXAMPLE 70Polymerization of THF with Diglycolyl
Chloride and Ytterbium Triflate

In a dry box, ytterbium triflate (1.00 g) was added
5 to a 100 mL RB flask equipped with a stirring bar. The
flask was sealed with a rubber septum and removed from
the dry box. A nitrogen purge was attached and THF
(20 mL) added via syringe, followed by diglycolyl
chloride (2.00 mL, 97%). After 60 minutes the
10 polymerization was terminated by the addition of water
(25 mL) and THF (25 mL) and ether (50 mL). The
separated organic phase was concentrated at reduced
pressure and then dried under vacuum. Polymer yield:
9.53 g.

EXAMPLE 71Polymerization of THF with Diglycolyl
Chloride and Zirconium Triflate

In a dry box, zirconium triflate (1.00 g) was added
to a 100 mL RB flask equipped with a stirring bar. The
20 flask was sealed with a rubber septum and removed from
the dry box. A nitrogen purge was attached and THF
(20 mL) added via syringe, followed by diglycolyl
chloride (2.00 mL, 97%). After 60 minutes the
polymerization was terminated by the addition of water
25 (25 mL) and THF (25 mL) and ether (50 mL). The
separated organic phase was concentrated at reduced
pressure and then dried under vacuum. Polymer yield:
7.32 g.

EXAMPLE 72

30 Copolymerization of THF/3-Methyl-THF
with Ytterbium Triflate and Adipoyl Chloride

In a dry box, ytterbium triflate (0.50 g) was added
an oven dried 100 mL RB flask equipped with a stirring
bar. The flask was sealed with a rubber septum and
35 removed from the dry box. After the attachment of a

nitrogen bleed THF (7.5 mL), 3-methyl-THF (2.5 mL) and adipoyl chloride (1.00 mL) were added to the flask. After 60 minutes the polymerization was terminated via the addition of water (25 mL), THF (50 mL) and ether (25 mL). The resulting organic phase was separated, concentrated at reduced pressure and then dried under vacuum. Polymer yield: 5.2 g.

EXAMPLE 73

Polymerization of THF with Scandium

Triflate and Acetic Anhydride

In a dry box, scandium triflate (0.75 g) was added to each of four separate oven dried 100 mL RB flasks equipped with stirring bars. The flasks were sealed with rubber septa and removed from the dry box. After the attachment of nitrogen bleeds THF (20 mL) and acetic anhydride (0.75 mL) were added to each flask. After 15, 30, 45 and 60 minutes, a polymerization was terminated via the addition of water (25 mL) and THF (50 mL). The resulting organic phases were separated, concentrated at reduced pressure and then dried under vacuum. Polymer yields and GPC analysis:

Polymer. Time	Polymer Yield (%)	Mn (PS STD)	Mw	PD
15 mins.	63.64	3780	11000	2.91
30 mins.	70.85	3270	9270	2.82
45 mins.	70.85	2780	9740	3.49
60 mins.	74.18	2930	8330	2.84

EXAMPLE 74

Polymerization of THF with Copper

Triflate and Acetic Anhydride

In a dry box, copper triflate (0.75 g) was added to each of four separate oven dried 100 mL RB flasks equipped with stirring bars. The flasks were sealed with rubber septa and then removed from the dry box. Nitrogen bleeds were attached and THF (20 mL) and acetic

anhydride (0.75 mL) were added to each flask. After 45, 60, 75 and 90 minutes a polymerization was terminated via the addition of water (25 mL) and THF (50 mL). The separated organic phases were separated, concentrated at reduced pressure and then dried under vacuum. Polymer yields and GPC analysis:

Polymer. Time	Polymer Yield (%)	Mn (PS STD)	Mw	PD
45 mins.	23.90	10500	21100	2.01
60 mins.	30.10	12000	23400	1.95
75 mins.	35.00	11400	23500	2.07
90 mins.	53.21	13900	25900	1.86

EXAMPLE 75

Polymerization of THF with Zirconium Triflate and Acetic anhydride

In a dry box, zirconium triflate (0.75 g) was added to each of four separate oven dried 100 mL RB flasks equipped with stirring bars. The flasks were sealed with rubber septa and removed from the dry box. Nitrogen bleeds were attached and THF (20 mL) and acetic anhydride (0.75 mL) were added to each flask. After 15, 30, 45 and 60 minutes, a polymerization was terminated via the addition of water (25 mL) and THF (50 mL). The resulting organic phases were separated, concentrated at reduced pressure and then dried under vacuum. Polymer yields:

Polymer. Time	Polymer Yield (%)
15 mins.	58.06
30 mins.	65.84
45 mins.	66.91
60 mins.	71.87

EXAMPLE 76Polymerization of THF with Tin
Triflate and Acetic Anhydride

In a dry box, tin triflate (0.75 g) was added to
5 each of four separate oven dried 100 mL RB flasks
equipped with stirring bars. The flasks were sealed
with rubber septa and removed from the dry box.
Nitrogen bleeds were attached and THF (20 mL) and acetic
anhydride (0.75 mL) were added to each flask. After 15,
10 30, 45 and 90 minutes, a polymerization was terminated
via the addition of water (25 mL) and THF (50 mL). The
resulting organic phases were separated, concentrated at
reduced pressure and then dried under vacuum. Polymer
yields:

Polymer. Time	Polymer Yield (%)
15 mins.	24.01
30 mins.	44.08
45 mins.	54.68
60 mins.	58.40

15

EXAMPLE 77Polymerization of THF with Zinc
Triflate and Acetic Anhydride

In a dry box, zinc triflate (0.75 g) was added to
an oven dried 100 mL RB flask equipped with a stirring
20 bar. The flask was sealed with a rubber septum and
removed from the dry box. A nitrogen bleed was attached
and THF (20 mL) and acetic anhydride (0.75 mL) were
added. After stirring overnight the polymerization was
terminated via the addition of water (25 mL) and THF
25 (50 mL). The resulting organic phase was separated,
concentrated at reduced pressure and then dried under
vacuum. Polymer Yield: 3.17 g (17.87%).

EXAMPLE 78Depolymerization of Polytetrahydrofuran
with Copper Triflate

Polytetrahydrofuran diol, $M_n = \sim 1,000$, and copper triflate (9 g) were placed in a 500 mL three neck flask equipped with a stirring bar, Vigreux column (12") and a fractional distillation head. A nitrogen purge was attached and all other openings were glass stoppered. The resulting mixture was heated by an oil bath and the resulting water clear distillate fractions collected as follow:

Fraction	Oil Bath Temp (°C)	Rxn Temp. (°C)	Head Temp. (°C)	Weight (g)
1	168	135-139	64	47.85
2	168	128-135	64	57.09
3	168	118-128	66	53.67
4	168	106-128	66	57.77
5	168	106	66	76.30

Total weight of distillate collected: 292.68 g

% Yield (Recovery): 97.56%

Total depolymerization time from start of collection to termination of experiment: 1 hr. 45 mins.

EXAMPLE 79Copolymerization of THF/3-Methyl-THF with
Zirconium Triflate and Acetic Anhydride

In a dry box, zirconium triflate (0.50 g) was added to an oven dried 100 mL RB flask equipped with a stirring bar. The flask was sealed with a rubber septum and removed from the dry box. A nitrogen bleed was attached and THF (7.5 mL) and 3-methyl-THF (2.5 mL) were added followed by acetic anhydride (1.00 mL). After 45 minutes the polymerization was terminated via the addition of water (25 mL) and THF (50 mL). The resulting organic phase was separated, concentrated at

reduced pressure and then dried under vacuum. Polymer yield: 5.68 g.

EXAMPLE 80

Copolymerization of THF/3-Methyl-THF with
Copper Triflate and Acetic Anhydride

5 In a dry box, copper triflate (0.50 g) was added to an oven dried 100 mL RB flask equipped with a stirring bar. The flask was sealed with a rubber septum and removed from the dry box. A nitrogen bleed was attached
10 and THF (7.5 mL) and 3-methyl-THF (2.5 mL) were added followed by acetic anhydride (1.00 mL). After 60 minutes the polymerization was terminated via the addition of water (25 mL) and THF (50 mL). The
15 resulting organic phase was separated, concentrated at reduced pressure and then dried under vacuum. Polymer yield: 2.48 g.

EXAMPLE 81

Copolymerization of THF/3-Methyl-THF
with Tin Triflate and Acetic Anhydride

20 In a dry box, tin triflate (0.50 g) was added to an oven dried 100 mL RB flask equipped with a stirring bar. The flask was sealed with a rubber septum and removed from the dry box. A nitrogen bleed was attached and THF (7.5 mL) and 3-methyl-THF (1.6 mL) were added followed
25 by acetic anhydride (1.00 mL). After 60 minutes the polymerization was terminated via the addition of water (25 mL) and THF (50 mL). The resulting organic phase was separated, concentrated at reduced pressure and then dried under vacuum. Polymer yield: 4.42 g.

EXAMPLE 82

Copolymerization of THF/3-Methyl-THF with
Scandium Triflate and Acetic Anhydride

35 In a dry box, scandium triflate (0.50 g) was added to an oven dried 100 mL RB flask equipped with a stirring bar. The flask was sealed with a rubber septum

and removed from the dry box. A nitrogen bleed was attached and THF (7.5 mL) and 3-methyl-THF (2.5 mL) were added followed by acetic anhydride (1.00 mL). After 45 minutes the polymerization was terminated via the
5 addition of water (25 mL) and THF (50 mL). The resulting organic phase was separated, concentrated at reduced pressure and then dried under vacuum. Polymer yield: 5.81 g.

EXAMPLE 83

10 Polymerization of THF with Copper Triflate and Trifluoroacetic Anhydride

In a dry box, copper triflate (1.00 g) was added to an oven dried 100 mL RB flask equipped with a stirring bar. The flask was sealed with a rubber septum and
15 removed from the dry box. A nitrogen bleed was attached and THF (20 mL) and trifluoroacetic anhydride (2.00 mL) were added. After stirring for 3 hrs. the polymerization was terminated via the addition of water (25 mL) and THF (50 mL). The resulting organic phase
20 was separated, concentrated at reduced pressure and then dried under vacuum. Polymer Yield: 7.5 g.

EXAMPLE 84

Polymerization of THF with Trifluoroacetic Acid and Ytterbium Triflate at 45°C

25 In a dry box, ytterbium triflate (5.00 g) was added to an oven dried 100 mL RB flask equipped with a stirring bar. The flask was sealed with rubber septa and removed from the dry box. After the attachment of nitrogen bleeds THF (20.00 mL) and trifluoroacetic acid
30 (4.00 mL) were added to the flask. Then flask was then immediately placed in an oil bath maintained at 45°C. After 120 minutes the polymerization was terminated via the addition of water (25 mL), THF (50 mL) and ether (25 mL). The resulting organic phase was separated,
35 concentrated at reduced pressure and then dried under

vacuum. Polymer yield: 6.61 g. GPC analysis (PS STD.): Mn = 5680, Mw = 9090, PD = 1.60.

EXAMPLE 85

Polymerization of THF with Trifluoroacetic
Acid and Ytterbium Triflate at 45°C

5 In a dry box, ytterbium triflate (5.00 g) was added to an oven dried 100 mL RB flask equipped with a stirring bar. The flask was sealed with rubber septa and removed from the dry box. After the attachment of a
10 nitrogen bleed THF (20.00 mL) and trifluoroacetic acid (5.00 mL) were added to the flask. The flask was then immediately placed in an oil bath maintained at 45°C. After 120 minutes the polymerization was terminated via the addition of water (25 mL), THF (50 mL) and ether
15 (25 mL). The resulting organic phase was separated, concentrated at reduced pressure and then dried under vacuum. Polymer yield: 3.07 g. GPC analysis (PS STD.): Mn = 3290, Mw = 4810, PD = 1.46.

EXAMPLE 86

Polymerization of THF with Trifluoroacetic
Acid and Ytterbium Triflate

20 In a dry box, ytterbium triflate (2.00, 3.00, 4.00 and 5.00 g) was added to each of four separate oven dried 100 mL RB flasks equipped with stirring bars. The
25 flasks were sealed with rubber septa and removed from the dry box. After the attachment of nitrogen bleeds THF (20.00 mL) and trifluoroacetic acid (2.00 mL) were added to each flask. After 90 minutes the polymerizations were terminated via the addition of water (25 mL),
30 THF (50 mL) and ether (25 mL). The resulting organic phases were separated, concentrated at reduced pressure and then dried under vacuum. Polymer yields and GPC analyses:

Ytterbium Triflate (g)	Polymer Yield (g)	Mn (PS STD.)	Mw	PD
2.00	5.32	60200	95600	1.59
3.00	5.95	58500	89400	1.53
4.00	6.70	46100	76700	1.66

EXAMPLE 87Polymerization of THF with Trifluoroacetic
Acid and Yttrium Triflate

In a dry box, yttrium triflate (3.00 g) was added
5 to each of three separate oven dried 100 mL RB flasks
equipped with stirring bars. The flasks were sealed
with rubber septa and removed from the dry box. After
the attachment of nitrogen bleeds THF (20.00 mL) and
trifluoroacetic acid (5.00 mL) were added to each flask.
10 After 120, 150 and 180 minutes a polymerization was
terminated via the addition of water (25 mL), THF
(50 mL) and ether (25 mL). The resulting organic phases
were separated, concentrated at reduced pressure and
then dried under vacuum. Polymer yields and GPC
15 analyses:

Polymer. Time	Polymer Yield (g)	Mn (PS STD.)	Mw	PD
120 mins.	1.57	22700	32900	1.45
150 mins.	2.75	24600	37900	1.54
180 mins.	3.69	30300	46400	1.54

EXAMPLE 88Polymerization of THF with Trifluoroacetic
Acid and Erbium Triflate

In a dry box, erbium triflate (4.00 g) was added to
20 each of five separate oven dried 100 mL RB flasks
equipped with stirring bars. The flasks were sealed
with rubber septa and removed from the dry box. After
the attachment of nitrogen bleeds THF (20.00 mL) and
trifluoroacetic acid (5.00 mL) were added to each flask.
25 After 60, 90, 120, 150 and 180 minutes a polymerization
was terminated via the addition of water (25 mL), THF

(50 mL) and ether (25 mL). The resulting organic phases were separated, concentrated at reduced pressure and then dried under vacuum. Polymer yields and GPC analyses:

Polymer. Time	Polymer Yield (g)	Mn (PD STD.)	Mw	PD
60 mins.	2.02	13300	20900	1.57
90 mins.	3.13	26500	36900	1.39
120 mins.	4.84	26600	39700	1.49
150 mins.	5.08	30600	49600	1.62
180 mins.	5.58	27900	45700	1.63

5

EXAMPLE 89Copolymerization of THF/3-Methyl-THF with
Trifluoroacetic Acid and Ytterbium Triflate

In a dry box, ytterbium triflate (5.00 g) was added to separate oven dried 100 mL RB flasks equipped with stirring bars. The flasks were sealed with rubber septa and removed from the dry box. After the attachment of nitrogen bleeds THF (15.00 mL and 3-methyl-THF (5.00 mL) were added to each flask. Trifluoroacetic acid (3 and 4 mL) was then added to each flask. After 120 minutes the polymerizations were terminated via the addition of water (25 mL), THF (50 mL) and ether (25 mL). The resulting organic phases were separated, concentrated at reduced pressure and then dried under vacuum. Polymer yields and GPC analyses:

Trifluoroacetic Acid	Polymer Yield (g)	Mn (PS STD.)	Mw	PD
3 mL	5.37	24500	37500	1.53
4 mL	3.9	20900	30300	1.45

20

EXAMPLE 90Polymerization of THF with Trifluoroacetic Anhydride/
Trifluoroacetic Acid and Ytterbium Triflate

In a dry box, ytterbium triflate (3.00 g) was added to each of four separate oven dried 100 mL RB flasks equipped with stirring bars. The flasks were sealed

25

with rubber septa and removed from the dry box. After the attachment of nitrogen bleeds THF (20.00 mL) was added to each flask. Trifluoroacetic anhydride and trifluoroacetic acid were added together via syringes in the ratios shown below. After 60 minutes the polymerizations were terminated via the addition of water (25 mL), THF (50 mL) and ether (25 mL). The resulting organic phases were separated, concentrated at reduced pressure and then dried under vacuum. Polymer yields and GPC analyses:

Trifluoroacetic Anhydride/ Trifluoroacetic Acid (mL)	Polymer Yield (g)	Mn (PS STD.)	Mw	PD
5/2	10.66	8090	13400	1.66
5/3	9.21	6600	10100	1.54
5/4	7.13	5200	8150	1.57
5/5	4.86	4200	59100	1.41

EXAMPLE 91

Polymerization of THF with Trifluoroacetic Anhydride/Trifluoroacetic Acid and Ytterbium Triflate

In a dry box, ytterbium triflate (3.00 g) was added to an oven dried 100 mL RB flask equipped with a stirring bar. The flask was sealed with a rubber septum and removed from the dry box. After the attachment of a nitrogen bleed THF (20.00 mL) was added to the flask. Trifluoroacetic anhydride (3.00 mL) and trifluoroacetic acid (5.00 mL) were added together via syringe. After 60 minutes the polymerization was terminated via the addition of water (25 mL), THF (50 mL) and ether (25 mL). The resulting organic phase was separated, concentrated at reduced pressure and then dried under vacuum. Polymer yield: 6.85 g. GPC analysis: Mn = 5910, Mw = 9970, PD = 1.50 (PS STD.).

EXAMPLE 92Polymerization of THF with Pentafluoropropionic
Acid and Ytterbium Triflate

In a dry box, ytterbium triflate (5.00 g) was added
5 to an oven dried 100 mL RB flask equipped with a
stirring bar. The flask was sealed with a rubber septum
and removed from the dry box. After the attachment of a
nitrogen bleed THF (20.00 mL) and pentafluoropropionic
acid (2.00 mL) were added via syringe. After 150
10 minutes the polymerization was terminated via the
addition of water (25 mL), THF (50 mL) and ether
(25 mL). The resulting organic phase was separated,
concentrated at reduced pressure and then dried under
vacuum. Polymer yield: 9.42 g. GPC analysis:
15 $M_n = 71500$, $M_w = 126000$, $PD = 1.77$ (PS STD.).

EXAMPLE 93Polymerization of THF with Pentafluoropropionic
Acid and Ytterbium Triflate

In a dry box, ytterbium triflate (5.00 g) was added
20 to an oven dried 100 mL RB flask equipped with a
stirring bar. The flask was sealed with a rubber septum
and removed from the dry box. After the attachment of a
nitrogen bleed THF (20.00 mL) and pentafluoropropionic
acid (5.00 mL) were added via syringe. After 150
25 minutes the polymerization was terminated via the
addition of water (25 mL), THF (50 mL) and ether
(25 mL). The resulting organic phase was separated,
concentrated at reduced pressure and then dried under
vacuum. Polymer yield: 7.00 g. GPC analysis:
30 $M_n = 20100$, $M_w = 38700$, $PD = 1.92$ (PS STD.).

EXAMPLE 94Polymerization of THF with Cyanoacetic Acid
and Ytterbium Triflate

In a dry box, ytterbium triflate (5.00 g) and
35 cyanoacetic acid (5.00 g) were added to an oven dried

100 mL RB flask equipped with a stirring bar. The flask was sealed with a rubber septum and removed from the dry box. After the attachment of a nitrogen bleed THF (20.00 mL) was added via syringe. After 150 minutes the
5 polymerization was terminated via the addition of water (25 mL), THF (50 mL) and ether (25 mL). The resulting organic phase was separated, concentrated at reduced pressure and then dried under vacuum. Polymer yield: 6.15 g. GPC analysis: $M_n = 22900$, $M_w = 33900$,
10 $PD = 1.48$ (PS STD.).

EXAMPLE 95

Polymerization of THF with Trifluoroacetic Acid and Aluminum Triflate

In a dry box, aluminum triflate (1.5 g) was added
15 to an oven dried 100 mL RB flask equipped with a stirring bar. The flask was sealed with a rubber septum and removed from the dry box. After the attachment of a nitrogen bleed THF (10 mL) and trifluoroacetic acid (1.5 mL) were added via syringe. After 120 minutes the
20 polymerization was terminated via the addition of water (25 mL), THF (50 mL) and ether (25 mL). The resulting organic phase was separated, concentrated at reduced pressure and then dried under vacuum. Polymer yield: 4.17 g. GPC analysis: $M_n = 28500$, $M_w = 52000$,
25 $PD = 1.82$ (PS STD.).

EXAMPLE 96

Polymerization of THF with Trifluoroacetic Acid and Zirconium Triflate

In a dry box, zirconium triflate (1.5 g) was added
30 to an oven dried 100 mL RB flask equipped with a stirring bar. The flask was sealed with a rubber septum and removed from the dry box. After the attachment of a nitrogen bleed THF (10 mL) and trifluoroacetic acid (1.5 mL) were added via syringe. After 120 minutes the
35 polymerization was terminated via the addition of water

(25 mL), THF (50 mL) and ether (25 mL). The resulting organic phase was separated, concentrated at reduced pressure and then dried under vacuum. Polymer yield: 5.63 g. GPC analysis: Mn = 33300, Mw = 52600, PD = 1.58 (PS STD.).

EXAMPLE 97

Polymerization of THF with Pentafluoropropionic Acid and Aluminum Triflate

In a dry box, aluminum triflate (2.5 g) was added to an oven dried 100 mL RB flask equipped with a stirring bar. The flask was sealed with a rubber septum and removed from the dry box. After the attachment of a nitrogen bleed THF (10.00 mL) and pentafluoropropionic acid (0.90 mL) were added via syringe. After 120 minutes the polymerization was terminated via the addition of water (25 mL), THF (50 mL) and ether (25 mL). The resulting organic phase was separated, concentrated at reduced pressure and then dried under vacuum. Polymer yield: 6.73 g. GPC analysis: Mn = 11700, Mw = 20600, PD = 1.76 (PS STD.).

EXAMPLE 98

Polymerization of THF with Chlorodifluoroacetic Acid and Zirconium Triflate

In a dry box, zirconium triflate (2.5 g) was added to an oven dried 100 mL RB flask equipped with a stirring bar. The flask was sealed with a rubber septum and removed from the dry box. After the attachment of a nitrogen bleed THF (10.00 mL) and chlorodifluoroacetic acid (2.50 mL) were added via syringe. After 120 minutes the polymerization was terminated via the addition of water (25 mL), THF (50 mL) and ether (25 mL). The resulting organic phase was separated, concentrated at reduced pressure and then dried under vacuum. Polymer yield: 5.55 g. GPC analysis: Mn = 19600, Mw = 35300, PD = 1.80 (PS STD.).

EXAMPLE 99Polymerization of THF with 4-Nitrobenzoic Acid
and Aluminum Triflate

In a dry box, aluminum triflate (1.50 g) and
5 4-nitrobenzoic acid (4.50 g) were added to an oven dried
100 mL RB flask equipped with a stirring bar. The flask
was sealed with a rubber septum and removed from the dry
box. After the attachment of a nitrogen bleed THF
(20.00 mL) was added via syringe. After 30 minutes the
10 polymerization was terminated via the addition of water
(25 mL), THF (50 mL) and ether (25 mL). The resulting
organic phase was washed with water (2 x 1000 mL),
separated, concentrated at reduced pressure and then
dried under vacuum. Polymer yield: 4.43 g. GPC
15 analysis: Mn = 37000, Mw = 51000, PD = 1.38 (PS STD.).

EXAMPLE 100Polymerization of THF with Trifluoroacetic
Acid and Yttrium Triflate

In a dry box, yttrium triflate (3.00 g) was added
20 to an oven dried 100 mL RB flask equipped with a
stirring bar. The flask was sealed with a rubber septum
and removed from the dry box. After the attachment of a
nitrogen bleed THF (20.00 mL) and trifluoroacetic acid
(5.00 mL) were added via syringe. After 180 minutes the
25 polymerization was terminated via the addition of water
(25 mL), THF (50 mL) and ether (25 mL). The resulting
organic phase was separated, concentrated at reduced
pressure and then dried under vacuum. Polymer yield:
3.69 g. GPC analysis: Mn = 30300, Mw = 46400,
30 PD = 1.54 (PS STD.).

EXAMPLE 101Copolymerization of THF/3-Methyl-THF with
Trifluoroacetic Acid and Ytterbium Triflate

In a dry box, ytterbium triflate (5.00 g) was added
35 to an oven dried 100 mL RB flask equipped with a

stirring bar. The flask was sealed with a rubber septum and removed from the dry box. After the attachment of a nitrogen bleed THF (15.00 mL), 3-methyl-THF (5.00 mL) and trifluoroacetic acid (3.00 mL) were added via
5 syringe. After 120 minutes the polymerization was terminated via the addition of water (25 mL), THF (50 mL) and ether (25 mL). The resulting organic phase was separated, concentrated at reduced pressure and then dried under vacuum. Polymer yield: 5.37 g. GPC
10 analysis: Mn = 24500, Mw = 37500, PD = 1.53 (PS STD.).

EXAMPLE 102

Polymerization of THF with Acetic Acid and Ytterbium Triflate

In a dry box, ytterbium triflate (5.00 g) was added
15 to each of four separate oven dried 100 mL RB flasks equipped with stirring bars. The flasks were sealed with rubber septa and removed from the dry box. After the attachment of nitrogen bleeds THF (20.00 mL) and acetic acid (5.00 mL) were added to each flask. After
20 3, 4, 5 and 24 hours a polymerization was terminated via the addition of water (25 mL), THF (50 mL) and ether (25 mL). The resulting organic phases were separated, washed with water (2 x 50 mL), concentrated at reduced pressure and then dried under vacuum. Polymer yields
25 and GPC analyses:

Polymer. Time (Hrs.)	Polymer Yield (g)	Mn (PS STD.)	Mw	PD
3	1.15	17900	34600	1.93
4	1.38	18400	33700	1.83
5	1.71	16400	34000	2.07
24	5.29	13000	30400	2.33

EXAMPLE 103Polymerization of THF with Formic Acid (96%)Acid and Ytterbium Triflate

In a dry box, ytterbium triflate (5.00 g) was added
5 to each of six separate oven dried 100 mL RB flasks
equipped with stirring bars. The flasks were sealed
with rubber septa and removed from the dry box. After
the attachment of nitrogen bleeds THF (20.00 mL) and
formic acid (96%, 0.75 mL) were added to each flask.
10 After 2, 3, 4, 5, 6 and 24 hours a polymerization was
terminated via the addition of water (25 mL), THF
(50 mL) and ether (25 mL). The resulting organic phases
were separated, washed with water (2 x 50 mL),
concentrated at reduced pressure and then dried under
15 vacuum. Polymer yields and GPC analyses:

Polymer. Time (Hrs.)	Polymer Yield (g)	Mn (PS STD.)	Mw	PD
2	1.25	14300	29500	2.06
3	1.65	15100	30300	2.00
4	2.27	17600	32700	1.88
5	2.72	16700	30800	1.85
6	3.29	15300	29800	1.95
24	7.93	10700	23100	2.16

EXAMPLE 104Polymerization of THF with Formic Acid (96%)Acid and Ytterbium Triflate

In a dry box, ytterbium triflate (15.77 g) was
20 added to each of six separate oven dried 100 mL RB
flasks equipped with stirring bars. The flasks were
sealed with rubber septa and removed from the dry box.
After the attachment of nitrogen bleeds THF (20.00 mL)
and formic acid (96%, 2.00 mL) were added to each flask.
25 After 2, 3, 4, 5, 6 and 24 hours a polymerization was
terminated via the addition of water (25 mL), THF
(50 mL) and ether (25 mL). The resulting organic phases

were separated, washed with water (2 x 50 mL), concentrated at reduced pressure and then dried under vacuum. Polymer yields and GPC analyses:

Polymer. Time (Hrs.)	Polymer Yield (g)	Mn (PS STD.)	Mw	PD
2	1.67	4350	10900	2.51
3	2.22	5560	12000	2.16
4	2.83	5320	12400	2.34
5	3.09	5460	12100	2.22
6	3.28	5390	11700	2.19
24	5.82	3050	7860	2.58

EXAMPLE 105

5 Polymerization of THF with Pyruvonitrile
 and Ytterbium Triflate

In a dry box, ytterbium triflate (3.00 g) was added to a 100 mL round bottom flask equipped with a stirring bar. The flask was sealed with a rubber septum and removed from the dry box. After the attachment of a nitrogen bleed THF (20.00 mL) was added followed by pyruvonitrile (95%, 2.00 mL). After 60 minutes the polymerization was terminated by the addition of water (10 mL), THF (25 mL) and diethyl ether (25 mL). The resulting organic phase was separated, concentrated at reduced pressure and then dried under vacuum. Polymer yield: 1.44 g. GPC analysis: $M_n = 52700$, $M_w = 67000$, $PD = 1.27$ (PS STD.).

EXAMPLE 106

20 Polymerization of THF with Acetic Acid/
Acetic Anhydride and Yttrium Triflate

In a dry box, yttrium triflate (1.00 g) was added to an oven dried 100 mL RB flask equipped with a stirring bar. The flask was sealed with a rubber septum and removed from the dry box. After the attachment of a nitrogen bleed THF (20.00 mL), acetic acid (2.00 mL) and acetic anhydride (2.00 mL) were added via syringe.

After 60 minutes the polymerization was terminated via the addition of water (25 mL), THF (50 mL) and ether (25 mL). The resulting organic phase was separated, concentrated at reduced pressure and then dried under vacuum. Polymer yield: 7.32 g. GPC analysis: Mn = 2470, Mw = 5250, PD = 2.13 (PS STD.).

EXAMPLE 107

Polymerization of THF with Trichloroacetic Acid and Aluminum Triflate

10 In a dry box, aluminum triflate (4.5 g) and trichloroacetic acid (4.5 g) were added to an oven dried 100 mL RB flask equipped with a stirring bar. The flask was sealed with a rubber septum and removed from the dry box. After the attachment of a nitrogen bleed THF 15 (10.00 mL) was added via syringe. After 120 minutes the polymerization was terminated via the addition of water (25 mL), THF (50 mL) and ether (25 mL). The resulting organic phase was washed with water (2 x 50 mL), separated, concentrated at reduced pressure and then 20 dried under vacuum. Polymer yield: 5.0 g. GPC analysis: Mn = 33500, Mw = 80100, PD = 2.39 (PS STD.).

EXAMPLE 108

Polymerization of THF with 11-Cyano-1-undecanoic Acid and Ytterbium Triflate

25 In a dry box, ytterbium triflate (10.00 g) and 11-cyano-1-undecanoic acid (5.00 g) were added to an oven dried 100 mL RB flask equipped with a stirring bar. The flask was sealed with a rubber septum and removed from the dry box. After the attachment of a nitrogen 30 bleed THF (20.00 mL) was added via syringe. After 6 hrs. the polymerization was terminated via the addition of water (25 mL), THF (50 mL) and ether (25 mL). The resulting organic phase was separated, washed with 5% sodium bicarbonate (2 x 25 mL), concentrated at reduced

pressure and then dried under vacuum. Polymer yield:
5.61 g.

EXAMPLE 109

Polymerization of THF with 4-Acetylbutyric Acid
and Ytterbium Triflate

5 In a dry box, ytterbium triflate (10.00 g) was
added to an oven dried 100 mL RB flask equipped with a
stirring bar. The flask was sealed with a rubber septum
and removed from the dry box. After the attachment of a
10 nitrogen bleed THF (20.00 mL) and 4-acetylbutyric
(1.00 mL) were added via syringe. After 90 minutes the
polymerization was terminated via the addition of water
(25 mL), THF (50 mL) and ether (25 mL). The resulting
organic phase was separated, washed with 5% sodium
15 bicarbonate (2 x 25 mL), concentrated at reduced
pressure and then dried under vacuum. Polymer yield:
3.25 g.

EXAMPLE 110

Polymerization of THF with Glycolic Acid
and Ytterbium Triflate

20 In a dry box, ytterbium triflate (10.00 g) and
glycolic acid (99%, 1.00 g) were added to an oven dried
100 mL RB flask equipped with a stirring bar. The flask
was sealed with a rubber septum and removed from the dry
25 box. After the attachment of a nitrogen bleed THF
(20.00 mL) was added via syringe. After 90 minutes the
polymerization was terminated via the addition of water
(25 mL), THF (50 mL) and ether (25 mL). The resulting
organic phase was separated, concentrated at reduced
30 pressure and then dried under vacuum. Polymer yield:
4.76 g.

EXAMPLE 111

Preparation of Bismuth Triflate

BiCl_3 (630 mg, 2 mmol) was slurried in CH_2Cl_2
35 (20 mL). Triflic acid (900 mg, 6 mmol) was added

dropwise, and the mixture was stirred overnight at room temperature. The solvent was removed to give 0.9 g of an off white solid. ^{19}F NMR ($\text{DMSO}-d_6$): δ -77.3.

EXAMPLE 112

5 Polymerization of THF with Bismuth
 Triflate and Acetic Anhydride

In a dry box, bismuth triflate (0.5 g) was added to an oven dried 100 mL RB flask equipped with a stirring bar. The flask was sealed with a rubber septum and removed from the dry box. A nitrogen bleed was attached and THF (10.00 mL) and acetic anhydride (1.00 mL) were added. After stirring for 60 minutes the polymerization was terminated via the addition of water (25 mL), ether (25 mL) and THF (50 mL). The resulting organic phase was separated, concentrated at reduced pressure and then dried under vacuum. Polymer Yield: 5.71 g. GPC analysis: $M_n = 8350$, $M_w = 12400$, $PD = 1.49$ (PS STD.).

EXAMPLE 113

Preparation of $\text{Zr}(\text{OSO}_2\text{CF}_3)_4 \cdot \text{Zr}(\text{OCOCH}_3)_4$

20 Solid $\text{Zr}(\text{OTf})_4$ (0.5 g) and $\text{Zr}(\text{CF}_3\text{CO}_2)_4$ (0.5 g) were mixed and THF (25 mL) was added. The mixture was stirred for 15 minutes at room temperature. The solvent was removed and 0.9 g of off white solid was collected. ^{19}F NMR (CDCl_3): δ -78.3, -76.2 ($\text{Zr}(\text{CF}_3\text{CO}_2)_4$ comes at δ -75.8).

EXAMPLE 114

Polymerization of THF with $\text{Zr}(\text{OSO}_2\text{CF}_3)_4 \cdot \text{Zr}(\text{OCOCH}_3)_4$
and Acetic Anhydride

30 In a dry box, $\text{Zr}(\text{OSO}_2\text{CF}_3)_4 \cdot \text{Zr}(\text{OCOCH}_3)_4$ (0.5 g) was added to an oven dried 100 mL RB flask equipped with a stirring bar. The flask was sealed with a rubber septum and removed from the dry box. A nitrogen bleed was attached and THF (10.00 mL) and acetic anhydride (1.00 mL) were added. After stirring for 60 minutes the polymerization was terminated via the addition of water

(25 mL), ether (25 mL) and THF (50 mL). The resulting organic phase was separated, concentrated at reduced pressure and then dried under vacuum. Polymer Yield: 5.01 g. GPC analysis: $M_n = 6900$, $M_w = 10500$, $PD = 1.53$ (PS STD.).

EXAMPLE 115

Preparation of Gold Triflate

AuBr₃ (0.90 g, 2.1 mmol) was slurried in CH₂Cl₂ (20 mL) and triflic acid (0.90 g, 6.3 mmol) was added dropwise. The mixture was stirred overnight at room temperature. The solvent was removed and 0.77 g of black solid was collected. ¹⁹F NMR (DMSO-d₆): δ -76.9.

EXAMPLE 116

Polymerization of THF with Gold(III)

Triflate and Acetic Anhydride

In a dry box, gold(III) triflate (0.5 g) was added to an oven dried 100 mL RB flask equipped with a stirring bar. The flask was sealed with a rubber septum and removed from the dry box. A nitrogen bleed was attached and THF (10.00 mL) and acetic anhydride (1.00 mL) were added. After stirring for 60 minutes the polymerization was terminated via the addition of water (25 mL), ether (25 mL) and THF (50 mL). The resulting organic phase was separated, concentrated at reduced pressure and then dried under vacuum. Polymer Yield: 6.04 g. GPC analysis: $M_n = 5240$, $M_w = 9060$, $PD = 1.73$ (PS STD.).

EXAMPLE 117

Preparation of Y(OSO₂CF₃)₂Cl

Solid Y(OTf)₃ (540 mg, 1 mmol) and YCl₃ (98 mg, 0.5 mmol) were mixed, and this mixture was poured into stirred THF (30 mL). The mixture became warm as the solid dissolved. The solution was stirred for 15 min, and the THF was removed. ¹⁹F NMR (DMSO-d₆): δ -77.3.

EXAMPLE 118Polymerization of THF with $Y(OSO_2CF_3)_2Cl$ and Acetic Anhydride

In a dry box, $Y(OSO_2CF_3)_2Cl$ (0.5 g) was added to an
oven dried 100 mL RB flask equipped with a stirring bar.
The flask was sealed with a rubber septum and removed
from the dry box. A nitrogen bleed was attached and THF
(10.00 mL) and acetic anhydride (1.00 mL) were added.
After stirring for 60 minutes the polymerization was
terminated via the addition of water (25 mL), ether
(25 mL) and THF (50 mL). The resulting organic phase
was separated, concentrated at reduced pressure and then
dried under vacuum. Polymer Yield: 2.95 g. GPC
analysis: $M_n = 7390$, $M_w = 12800$, $PD = 1.73$ (PS STD.).

EXAMPLE 119Preparation of $Y(OSO_2CF_3)Cl_2$

Solid $Y(OTf)_3$ (540 mg, 1 mmol) and YCl_3 (390 mg,
2 mmol) were mixed, and this mixture was poured into
stirred THF (30 mL). The mixture became warm as the
solid dissolved. The solution was stirred for 15 min,
and the THF was removed. ^{19}F NMR ($DMSO-d_6$): $\delta -77.2$

EXAMPLE 120Polymerization of THF with $Y(OSO_2CF_3)Cl_2$ and Acetic Anhydride

In a dry box, $Y(OSO_2CF_3)Cl_2$ (0.5 g) was added to an
oven dried 100 mL RB flask equipped with a stirring bar.
The flask was sealed with a rubber septum and removed
from the dry box. A nitrogen bleed was attached and THF
(10.00 mL) and acetic anhydride (1.00 mL) were added.
After stirring for 60 minutes the polymerization was
terminated via the addition of water (25 mL), ether
(25 mL) and THF (50 mL). The resulting organic phase
was separated, concentrated at reduced pressure and then
dried under vacuum. Polymer Yield: 0.09 g.

EXAMPLE 121Preparation of Ta(OSO₂CF₃)₄OCH₂CH₃

Ta(OEt)₅ (813 mg, 2 mmol) was dissolved in CH₂Cl₂ (20 mL). Triflic acid (1.5 g, 10 mol) was added dropwise and the solution stirred overnight at room temperature. The solvent was removed to produce a colorless oil. ¹H and ¹⁹F NMR show a mixture of compounds. ¹H NMR (CDCl₃): δ 1.85 (t), 1.9 (t), 4.1, (q), 4.15 (broad, q).

EXAMPLE 122Polymerization of THF with Ta(OSO₂CF₃)₄OCH₂CH₃ and Acetic Anhydride

In a dry box, Ta(OSO₂CF₃)₄OCH₂CH₃ (0.5 g) was added to an oven dried 100 mL RB flask equipped with a stirring bar. The flask was sealed with a rubber septum and removed from the dry box. A nitrogen bleed was attached and THF (10.00 mL) and acetic anhydride (1.00 mL) were added. After stirring for 60 minutes the polymerization was terminated via the addition of water (25 mL), ether (25 mL), and THF (50 mL). The resulting organic phase was separated, concentrated at reduced pressure and then dried under vacuum. Polymer Yield: 6.29 g. GPC analysis: Mn = 2320, Mw = 5400, PD = 2.33 (PS STD.).

EXAMPLE 123Preparation of Iron(III) Bis-triflate-acetylacetonate

Fe(acac)₃ (1.0 g, 2.8 mmol) was dissolved in CH₂Cl₂ (15 mL), and triflic acid (850 mg, 5.7 mmol) was added dropwise. The purple solution was stirred overnight at room temperature. The solvent was removed to give a dark oil.

EXAMPLE 124Polymerization of THF with Iron(III)
Bis-Triflate-Acetylacetonate and Acetic Anhydride

In a dry box, iron(III) bis-triflate-acetyl-
5 acetate (0.5 g) was added to an oven dried 100 mL RB
flask equipped with a stirring bar. The flask was
sealed with a rubber septum and removed from the dry
box. A nitrogen bleed was attached and THF (10.00 mL)
and acetic anhydride (1.00 mL) were added. After
10 stirring for 60 minutes the polymerization was
terminated via the addition of water (25 mL), ether
(25 mL) and THF (50 mL). The resulting organic phase
was separated, concentrated at reduced pressure and then
dried under vacuum. Polymer Yield: 5.63 g. GPC
15 analysis: $M_n = 8330$, $M_w = 16100$, $PD = 1.94$ (PS STD.).

EXAMPLE 125Preparation of Ruthenium(III) Triflate

$RuCl_3$ (1.0 g, 4.6 mmol) was slurried in CH_2Cl_2
(20 mL) and triflic acid (2.0 g, 13.6 mmol) was added
20 dropwise. The mixture was stirred at room temperature
overnight. The solvent was removed and 1.15 g of black
solid was collected. ^{19}F NMR ($CDCl_3$): $\delta -76.7$.

EXAMPLE 126Polymerization of THF with Ruthenium(III) Triflate
25 and Acetic Anhydride

In a dry box, ruthenium(III) triflate (0.5 g) was
added to an oven dried 100 mL RB flask equipped with a
stirring bar. The flask was sealed with a rubber septum
and removed from the dry box. A nitrogen bleed was
30 attached and THF (10.00 mL) and acetic anhydride
(1.00 mL) were added. After stirring for 30 minutes the
polymerization was terminated via the addition of water
(25 mL), ether (25 mL) and THF (50 mL). The resulting
organic phase was separated, concentrated at reduced
35 pressure and then dried under vacuum. Polymer Yield:

5.25 g. GPC analysis: $M_n = 7960$, $M_w = 12400$, $PD = 1.56$ (PS STD.).

EXAMPLE 127

Preparation of Palladium(II) Triflate

5 $PdCl_2$ (1.0 g, 5.6 mmol) was slurried in CH_2Cl_2 (20 mL) and triflic acid (1.7 g, 11.3 mmol) was added dropwise. The mixture was stirred at room temperature overnight. The solvent was removed and 0.9 g of rust color solid was collected. ^{19}F NMR ($CDCl_3$): δ -78.5.

10

EXAMPLE 128

Polymerization of THF with Palladium(II) Triflate and Acetic Anhydride

15 In a dry box, palladium(II) triflate (0.5 g) was added to an oven dried 100 mL RB flask equipped with a stirring bar. The flask was sealed with a rubber septum and removed from the dry box. A nitrogen bleed was attached and THF (10.00 mL) and acetic anhydride (1.00 mL) were added. After stirring for 60 minutes the polymerization was terminated via the addition of water (25 mL), ether (25 mL) and THF (50 mL). The resulting organic phase was separated, concentrated at reduced pressure and then dried under vacuum. Polymer Yield: 0.73 g. GPC analysis: $M_n = 27100$, $M_w = 32500$, $PD = 1.20$ (PS STD.).

25

EXAMPLE 129

Polymerization of THF with Niobium(V) Triflate and Acetic Anhydride

30 In a dry box, niobium(V) triflate (0.5 g) was added to an oven dried 100 mL RB flask equipped with a stirring bar. The flask was sealed with a rubber septum and removed from the dry box. A nitrogen bleed was attached and THF (10.00 mL) and acetic anhydride (1.00 mL) were added. After stirring for 60 minutes the polymerization was terminated via the addition of water (25 mL), ether (25 mL) and THF (50 mL). The resulting

35

organic phase was separated, concentrated at reduced pressure and then dried under vacuum. Polymer Yield: 6.41 g. GPC analysis: $M_n = 1580$, $M_w = 5810$, $PD = 3.67$ (PS STD.).

5

EXAMPLE 130Polymerization of THF with Tungsten(VI)
Triflate and Acetic Anhydride

In a dry box, tungsten(VI) triflate (0.5 g) was added to an oven dried 100 mL RB flask equipped with a stirring bar. The flask was sealed with a rubber septum and removed from the dry box. A nitrogen bleed was attached and THF (10.00 mL) and acetic anhydride (1.00 mL) were added. After stirring for 60 minutes the polymerization was terminated via the addition of water (25 mL), ether (25 mL) and THF (50 mL). The resulting organic phase was separated, concentrated at reduced pressure and then dried under vacuum. Polymer Yield: 6.12 g. GPC analysis: $M_n = 4430$, $M_w = 8330$, $PD = 1.88$ (PS STD.).

20

EXAMPLE 131Preparation of Rhenium(V) Triflate

$ReCl_5$ (1.0 g, 2.75 mmol) was slurried in CH_2Cl_2 (25 mL) and triflic acid (2.1 g, 13.7 mmol) was added dropwise. The mixture was stirred overnight at room temperature. The solvent was removed and 0.9 g of black solid was collected. ^{19}F NMR ($CDCl_3$): δ -74.4, -76.3 (small peak).

25

EXAMPLE 132Polymerization of THF with Rhenium(V)
Triflate and Acetic Anhydride

30

In a dry box, rhenium(V) triflate (0.5 g) was added to an oven dried 100 mL RB flask equipped with a stirring bar. The flask was sealed with a rubber septum and removed from the dry box. A nitrogen bleed was attached and THF (10.00 mL) and acetic anhydride

35

(1.00 mL) were added. After stirring for 60 minutes the polymerization was terminated via the addition of water (25 mL), ether (25 mL) and THF (50 mL). The resulting organic phase was separated, concentrated at reduced pressure and then dried under vacuum. Polymer Yield: 5.60 g. GPC analysis: $M_n = 7170$, $M_w = 13500$, $PD = 1.89$ (PS STD.).

EXAMPLE 133

Preparation of Chromium(II) Triflate

CrCl₂ (0.62 g, 5 mmol) was slurried in CH₂Cl₂ (20 mL) and triflic acid (2.3 g, 15 mmol) was added dropwise. The mixture was stirred overnight at room temperature. The solvent was removed and 1.25 g of gray solid was collected. ¹⁹F NMR (DMSO-d₆): δ -76.65, -76.72.

EXAMPLE 134

Polymerization of THF with Chromium(II) Triflate and Acetic Anhydride

In a dry box, chromium(II) triflate (0.5 g) was added to an oven dried 100 mL RB flask equipped with a stirring bar. The flask was sealed with a rubber septum and removed from the dry box. A nitrogen bleed was attached and THF (10.00 mL) and acetic anhydride (1.00 mL) were added. After stirring for 60 minutes the polymerization was terminated via the addition of water (25 mL), ether (25 mL) and THF (50 mL). The resulting organic phase was separated, concentrated at reduced pressure and then dried under vacuum. Polymer Yield: 4.87 g. GPC analysis: $M_n = 9210$, $M_w = 18800$, $PD = 2.05$ (PS STD.).

EXAMPLE 135

Preparation of *n*-Cyclopentadienyl-tris(trifluoromethanesulfonato)zirconium

Cp*ZrCl₃ (1.0 g, 3 mmol) was slurried in CH₂Cl₂ (40 mL). THF (10.00 mL) was added to dissolve the

yellow solid. Solid AgOTf (2.3 g, 9 mmol) was added; a white solid formed immediately. The mixture was stirred 15 min, and the orangish solution was filtered. The solvent was removed to produce an orangish oil. The material was crystallized from ether and 1.1 g of yellow solid was collected. ^1H NMR showed several peaks around 2 ppm. Coordinated THF is observed by ^1H NMR (near δ 3.5 and 1.2).

EXAMPLE 136

10 Polymerization of THF with *n*-pentamethyl-
cyclopentadienyl-tris-(trifluoromethanesulfonato)-
zirconium and Acetic Anhydride

In a dry box, *n*-pentamethylcyclopentadienyl-tris-(trifluoromethanesulfonato)zirconium (0.5 g) was added to an oven dried 100 mL RB flask equipped with a stirring bar. The flask was sealed with a rubber septum and removed from the dry box. A nitrogen bleed was attached and THF (10.00 mL) and acetic anhydride (1.00 mL) were added. After stirring for 60 minutes the polymerization was terminated via the addition of water (25 mL), ether (25 mL) and THF (50 mL). The resulting organic phase was separated, concentrated at reduced pressure and then dried under vacuum. Polymer Yield: 6.49 g. GPC analysis: $M_n = 4350$, $M_w = 7930$, PD = 1.82 (PS STD.).

EXAMPLE 137

Preparation of Strontium Triflate

SrCl₂ (790 mg, 5 mmol) was slurried in CH₂Cl₂ (20 mL) and triflic acid (1.5 g, 10 mmol) was added dropwise. The mixture was stirred overnight at room temperature. The solvent was removed and 1.7 g of white solid was collected. ^{19}F NMR (DMSO-*d*₆): δ -77.4.

EXAMPLE 138Polymerization of THF with Strontium
Triflate and Acetic Anhydride

In a dry box, strontium triflate (0.5 g) was added
5 to an oven dried 100 mL RB flask equipped with a
stirring bar. The flask was sealed with a rubber septum
and removed from the dry box. A nitrogen bleed was
attached and THF (10.00 mL) and acetic anhydride
(1.00 mL) were added. After stirring for 60 minutes the
10 polymerization was terminated via the addition of water
(25 mL), ether (25 mL) and THF (50 mL). The resulting
organic phase was separated, concentrated at reduced
pressure and then dried under vacuum. Polymer Yield:
5.44 G. GPC analysis: $M_n = 6630$, $M_w = 11500$, $PD = 1.73$
15 (PS STD.).

EXAMPLE 139Preparation of $Cp_2(OTf)Zr-O-Zr(OTf)Cp_2$

$Cp_2Zr(Cl)-O-(Cl)ZrCp_2$ (1.3 g, 2.5 mmol) was
dissolved in CH_2Cl_2 (40 mL), and AgOTf (1.3 g, 5 mmol)
20 was added. The mixture was stirred over a weekend. The
mixture was filtered and the solvent was removed. A
white solid formed as the solvent evaporated. The
mixture was filtered and the solid was washed with Et_2O .
1.4 g of white solid was collected. 1H NMR
25 (toluene- d_8): δ 6.0 (s).

EXAMPLE 140Polymerization of THF with $Cp_2(OTf)Zr-O-Zr(OTf)Cp_2$
and Acetic Anhydride

In a dry box, $Cp_2(OTf)Zr-O-Zr(OTf)Cp_2$ (0.5 g) was
30 added to an oven dried 100 mL RB flask equipped with a
stirring bar. The flask was sealed with a rubber septum
and removed from the dry box. A nitrogen bleed was
attached and THF (10.00 mL) and acetic anhydride
(1.00 mL) were added. After stirring for 60 minutes the
35 polymerization was terminated via the addition of water

(25 mL), ether (25 mL) and THF (50 mL). The resulting organic phase was separated, concentrated at reduced pressure and then dried under vacuum. Polymer Yield: 1.84 g. GPC analysis: $M_n = 22600$, $M_w = 28800$, PD = 1.28 (PS STD.).

EXAMPLE 141

Polymerization of THF with $Cp_2MeZr(THF)BPh_4$ and Acetic Anhydride

In a dry box, $Cp_2MeZr(THF)BPh_4$ (0.5 g) was added to an oven dried 100 mL RB flask equipped with a stirring bar. The flask was sealed with a rubber septum and removed from the dry box. A nitrogen bleed was attached and THF (10.00 mL) and acetic anhydride (1.00 mL) were added. After stirring for 60 minutes the polymerization was terminated via the addition of water (25 mL), ether (25 mL) and THF (50 mL). The resulting organic phase was separated, concentrated at reduced pressure and then dried under vacuum. Polymer Yield: 0.78 g. GPC analysis: $M_n = 4840$, $M_w = 7390$, PD = 1.53 (PS STD.).

EXAMPLE 142

Preparation of Bis-(*n*-Cyclopentadienyl)-bis(trifluoromethanesulfonato)molybdenum

Solid Cp_2MoCl_2 (500 mg, 1.7 mmol) and AgOTf (0.91 g, 3.5 mmol) were mixed and CH_2Cl_2 (30 mL). The mixture stirred overnight at room temperature. The white solid was filtered off and the solvent was evaporated to give 300 mg of a green solid. 1H NMR ($CDCl_3$): δ 6.4 (s).

EXAMPLE 143

Polymerization of THF with Bis-(*n*-Cyclopentadienyl)-bis-(trifluoromethanesulfonato)molybdenum and Acetic Anhydride

In a dry box, bis-(*n*-Cyclopentadienyl)-bis-(trifluoromethanesulfonato)molybdenum (0.275 g) was added to an oven dried 100 mL RB flask equipped with a

stirring bar. The flask was sealed with a rubber septum and removed from the dry box. A nitrogen bleed was attached and THF (10.00 mL) and acetic anhydride (1.00 mL) were added. After stirring for 60 minutes the polymerization was terminated via the addition of water (25 mL), ether (25 mL) and THF (50 mL). The resulting organic phase was separated, concentrated at reduced pressure and then dried under vacuum. Polymer Yield: 0.77 g. GPC analysis: $M_n = 15000$, $M_w = 21600$, PD = 1.44 (PS STD.).

EXAMPLE 144

Preparation of Bis(trifluoromethanesulfonato)-bis(acetylacetonate)zirconium

Zr(acac)₄ (1.46 g, 3 mmol) was dissolved in CH₂Cl₂ (5 mL). A solution of triflic acid (0.9 g, 6 mmol) in CH₂Cl₂ (1 mL) was added to the Zr(acac)₄ solution. The solution was stirred 2 hours at room temperature. The solvent was removed and 1.79 g of yellow solid was collected. ¹⁹F NMR (CDCl₃): δ -78.4; ¹H NMR (CDCl₃): δ 2.15 (s), 5.82 (broad).

EXAMPLE 145

Polymerization of THF with Bis(trifluoromethanesulfonato)-bis(acetylacetonate)zirconium and Acetic Anhydride

In a dry box, bis(trifluoromethanesulfonato)-bis(acetylacetonate)zirconium (0.50 g) was added to an oven dried 100 mL RB flask equipped with a stirring bar. The flask was sealed with a rubber septum and removed from the dry box. A nitrogen bleed was attached and THF (10.00 mL) and acetic anhydride (1.00 mL) were added. After stirring for 60 minutes the polymerization was terminated via the addition of water (25 mL), ether (25 mL) and THF (50 mL). The resulting organic phase was separated, concentrated at reduced pressure and then

dried under vacuum. Polymer Yield: 5.27 g. GPC analysis: Mn = 13400, Mw = 20200, PD = 1.51 (PS STD.).

EXAMPLE 146

5 Preparation of Yttrium Bis(trifluoromethane-sulfonato)-2,2,6,6-tetramethyl-3,5-heptanedionate
 (t-Buacac)₃Y (0.64 g, 1 mmol) was dissolved in CH₂Cl₂ (5 mL). A solution of triflic acid (0.3 g, 2 mmol) in CH₂Cl₂ (1 mL) was added and the solution was stirred 2 hours at room temperature. The solvent was
10 removed and a white solid was collected. ¹H NMR (CDCl₃): δ 1.2, 1.1 (broad s); ¹⁹F NMR (CDCl₃): δ -78.4.

EXAMPLE 147

Polymerization of THF with Yttrium
15 Bis(trifluoromethanesulfonato)-2,2,6,6-tetramethyl-3,5-heptanedionate and Acetic Anhydride
 In a dry box, yttrium bis(trifluoromethane-sulfonato)-2,2,6,6-tetramethyl-3,5-heptanedionate (0.50 g) was added to an oven dried 100 mL RB flask
20 equipped with a stirring bar. The flask was sealed with a rubber septum and removed from the dry box. A nitrogen bleed was attached and THF (10.00 mL) and acetic anhydride (1.00 mL) were added. After stirring for 60 minutes the polymerization was terminated via the
25 addition of water (25 mL), ether (25 mL) and THF (50 mL). The resulting organic phase was separated, concentrated at reduced pressure and then dried under vacuum. Polymer Yield: 1.26 g. GPC analysis: Mn = 17200, Mw = 25300, PD = 1.47 (PS STD.).

30 EXAMPLE 148

Preparation of Yttrium Trifluoromethane-sulfonato-bis(2,2,6,6-tetramethyl-3,5-heptanedionate)
 (t-Buacac)₃Y (0.64 g, 1 mmol) was dissolved in
35 CH₂Cl₂ (5 mL). A solution of triflic acid (0.15 g,

1 mmol) in CH_2Cl_2 (1 mL) was added dropwise and the solution was stirred 2 h at room temperature. The solvent was removed and a white solid was collected. ^1H NMR (CDCl_3): δ 1.15, 1.02; ^{19}F NMR (CDCl_3): δ -78.6

5 (small, broad), -76.7.

EXAMPLE 149

Polymerization of THF with Yttrium Trifluoromethanesulfonato-bis(2,2,6,6-tetramethyl-3,5-heptanedionate) and Acetic Anhydride

10 In a dry box, yttrium trifluoromethanesulfonato-bis(2,2,6,6-tetramethyl-3,5-heptanedionate) (0.50 g) was added to an oven dried 100 mL RB flask equipped with a stirring bar. The flask was sealed with a rubber septum and removed from the dry box. A nitrogen bleed was
15 attached and THF (10.00 mL) and acetic anhydride (1.00 mL) were added. After stirring for 60 minutes the polymerization was terminated via the addition of water (25 mL), ether (25 mL) and THF (50 mL). The resulting organic phase was separated, concentrated at reduced
20 pressure and then dried under vacuum. Polymer Yield: 0.18 g.

EXAMPLE 150

Preparation of $\text{VO}(\text{OTf})_n(\text{OCHMe}_2)_{3-n}$

$\text{V}(\text{O})(\text{OnPr})_3$ (1.2 g, 5 mmol) was dissolved in CH_2Cl_2
25 (30 mL). Triflic acid (2.2 g, 15 mmol) was added dropwise to produce a dark red solution. The solvent was removed and a dark oil was produced.

EXAMPLE 151

Polymerization of THF with $\text{VO}(\text{OTf})_n(\text{OCHMe}_2)_{3-n}$ and Acetic Anhydride

30 In a dry box, $\text{VO}(\text{OTf})_n(\text{OCHMe}_2)_{3-n}$ (0.50 g) was added to an oven dried 100 mL RB flask equipped with a stirring bar. The flask was sealed with a rubber septum and removed from the dry box. A nitrogen bleed was
35 attached and THF (10.00 mL) and acetic anhydride

(1.00 mL) were added. After stirring for 60 minutes the polymerization was terminated via the addition of water (25 mL), ether (25 mL) and THF (50 mL). The resulting organic phase was separated, concentrated at reduced
5 pressure and then dried under vacuum. Polymer Yield: 6.07 g. GPC analysis: $M_n = 4770$, $M_w = 29110$, $PD = 1.91$ (PS STD.).

EXAMPLE 152

Preparation of Silicon Triflate

10 $SiCl_4$ (3 g, 17.6 mmol) was dissolved in CH_2Cl_2 (75 mL) and triflic acid (10.6 g, 70.7 mmol) was added dropwise. The mixture was stirred at room temperature over the weekend. The solvent was removed and 4.8 g of brown liquid was collected. ^{19}F NMR ($DMSO-d_6$): δ -76.4
15 (intense), small broad peaks at -77.8 and -77.95.

EXAMPLE 153

Polymerization of THF with Silicon Triflate and Acetic Anhydride

In a dry box, silicon triflate (0.50 g) was added
20 to an oven dried 100 mL RB flask equipped with a stirring bar. The flask was sealed with a rubber septum and removed from the dry box. A nitrogen bleed was attached and THF (10.00 mL) and acetic anhydride (1.00 mL) were added. After stirring for 60 minutes the
25 polymerization was terminated via the addition of water (25 mL), ether (25 mL) and THF (50 mL). The resulting organic phase was separated, concentrated at reduced pressure and then dried under vacuum. Polymer Yield: 7.76 g. GPC analysis: $M_n = 1450$, $M_w = 3170$, $PD = 2.18$
30 (PS STD.).

EXAMPLE 154

Polymerization of 1,3-Dioxolane with Ytterbium Triflate

In a dry box, ytterbium triflate (1.5 g) was added
35 to an oven dried 100 mL RB flask equipped with a

stirring bar. The flask was sealed with a rubber septum and removed from the dry box. After the attachment of nitrogen bleeds 1,3-dioxolane (10.00 mL) was added to the flask. After 60 minutes the polymerization was
5 terminated via the addition of water (25 mL), THF (50 mL) and ether (25 mL). The resulting aqueous phase was separated, concentrated at reduced pressure and then dried under vacuum. Yield: 8.89 g (no attempt was made to remove the catalyst from the polymer). GPC analysis
10 (PS STD.): $M_n = 4170$, $M_w = 8550$, $PD = 2.05$.

EXAMPLE 155

Polymerization of 1,3,5-Trioxane with Ytterbium Triflate

In a dry box, ytterbium triflate (1.5 g) was added
15 to an oven dried 100 mL RB flask equipped with a stirring bar. In a separate 100 mL RB flask 1,3,5-trioxane (20.00 g) was added. The flasks were sealed with a rubber septum and removed from the dry box. To the flask containing the trioxane cyclohexane
20 (20 mL) was added, and the resulting mixture heating to 60°C via an oil bath until an homogeneous solution resulted. This solution (20.00 mL) was then added via syringe to the flask with ytterbium triflate at this temperature. The resulting mixture was then placed in
25 an oil bath maintained at 60°C. After 60 minutes, the polymerization was terminated by the addition of water (25 mL) and ether (25 mL). The resulting solid was separated and dried under vacuum, giving 4.74 g of
polymer.

30

EXAMPLE 156

Polymerization of THF with N-Acetylglycine and Ytterbium Triflate

In a dry box, ytterbium triflate (10.00 g) and
N-acetylglycine (2.00 g) were added to an oven dried
35 100 mL RB flask equipped with a stirring bar. The flask

was sealed with a rubber septum and removed from the dry box. After the attachment of a nitrogen bleed THF (20.00 mL) was added via syringe. After 180 minutes the polymerization was terminated via the addition of water (25 mL), THF (50 mL) and ether (25 mL). The resulting organic phase was separated, concentrated at reduced pressure and then dried under vacuum. Polymer yield: 5.27 g (29.7%). GPC analysis: Mn = 20500, Mw = 43700, PD = 2.13 (PS STD.).

EXAMPLE 157

Polymerization of THF with

N-Acetyl-DL-tryptophan and Ytterbium Triflate

In a dry box, ytterbium triflate (5.00 g) and N-acetyl-DL-tryptophan (1.00 g) were added to an oven dried 100 mL RB flask equipped with a stirring bar. The flask was sealed with a rubber septum and removed from the dry box. After the attachment of a nitrogen bleed THF (20.00 mL) was added via syringe.. After 26 hrs. the polymerization was terminated via the addition of water (25 mL), THF (50 mL) and ether (25 mL). The resulting organic phase was separated, concentrated at reduced pressure and then dried under vacuum. Polymer yield: 7.13 g. GPC analysis: Mn = 40200, Mw = 92100, PD = 2.29 (PS STD.).

WHAT IS CLAIMED IS:

1. A process for the polymerization of cyclic ethers, comprising, contacting one or more oxiranes, oxetanes, tetrahydrofurans, oxepanes, 1,3-dioxolanes or
5 1,3,5-trioxanes with a compound of the formula $MZ_s \cdot Q_t$, and an accelerator selected from the group consisting of carboxylic acids whose pKa in water is less than 6, carboxylic anhydrides and acyl halides, wherein:

- M is a metal selected from the group
10 consisting of cobalt, vanadium, niobium, tungsten, strontium, barium, scandium, yttrium, the rare earth metals, titanium, zirconium, hafnium, chromium, molybdenum, tantalum, rhenium, iron, ruthenium, osmium, rhodium, iridium, palladium, platinum, silver, gold,
15 zinc, cadmium, mercury, aluminum, gallium, indium, thulium, germanium, tin, lead, arsenic, antimony and bismuth;

- at least one of Z is an anion of the formula $^{-}OSO_2R^5$, wherein R^5 is perfluoroalkyl containing 1 to 12
20 carbon atoms or part of a fluorinated polymer wherein the carbon atoms alpha and beta to the sulfonate group are together bonded to at least four fluorine atoms, or tetraphenylborate, and the remainder of Z is oxo or one or more monovalent anions;

- 25 s is 2 when M is strontium, barium, cobalt, rhodium,, iridium, palladium, platinum, chromium, zinc, cadmium or mercury;

- s is 3 when M is scandium, yttrium, a rare earth metal, arsenic, antimony, bismuth, gold, iron,
30 ruthenium, osmium, aluminum, gallium, indium or thulium;

- s is 4 when M is titanium, zirconium, hafnium, molybdenum, germanium, tin, or lead;

- s is 5 when M is rhenium, vanadium, niobium or tantalum;

- 35 s is 6 when M is tungsten;

Q is a neutral ligand;

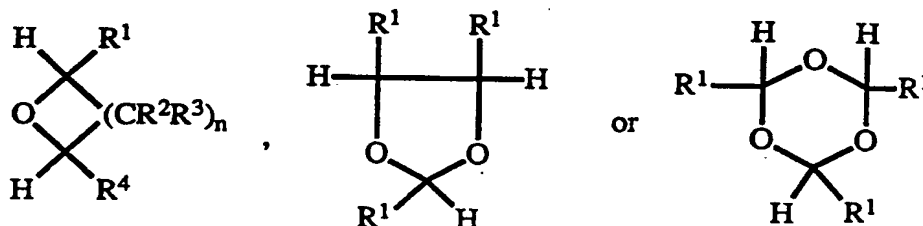
t is 0 or an integer of 1 to 6;

and provided that each oxo group present as part of Z is considered to account for two of s.

2. The process as recited in Claim 1 wherein said cyclic ether is one or more of said tetrahydrofurans, oxepanes, 1,3-dioxolanes or 1,3,5-trioxanes.

3. The process as recited in Claim 2 wherein M is a metal selected from the group consisting of strontium, barium, scandium, yttrium, the rare earth metals, titanium, zirconium, hafnium, chromium, molybdenum, tantalum, rhenium, iron, ruthenium, osmium, rhodium, iridium, palladium, platinum, silver, gold, zinc, cadmium, mercury, germanium, tin, lead, arsenic, antimony and bismuth.

4. The process as recited in Claim 3 wherein said cyclic ether comprises the formula



wherein:

each R^1 , R^2 , R^3 and R^4 is independently hydrogen or hydrocarbyl containing 1 to 20 carbon atoms; and

n is 2 or 4.

5. The process as recited in Claim 4 wherein n is 2 and R^1 , R^4 and all of R^2 and R^3 are hydrogen.

6. The process as recited in Claim 4 wherein n is 2 and R^1 and R^4 are each hydrogen, one of R^2 is hydrogen, the other R^2 is methyl, and both R^3 are hydrogen.

7. The process as recited in Claim 3 wherein R⁵ is trifluoromethyl or perfluoroalkyl.

8. The process as recited in Claim 5 wherein M is strontium, scandium, yttrium, the rare earth metals, titanium, zirconium, hafnium, vanadium, niobium, tantalum, chromium, molybdenum, tungsten, rhenium, iron, ruthenium, palladium, copper, gold, zinc, tin, bismuth or mischmetall.

9. The process as recited in Claim 1 carried out at a temperature of about -80°C to about 130°C.

10. The process as recited in Claim 1 wherein said carboxylic acid is trifluoroacetic acid, formic, acetic, cyanoacetic, nitropropionic, acrylic, methacrylic acid, N-acetylglycine or N-acetyltryptophan.

11. The process as recited in Claim 1 wherein said carboxylic anhydride is acetic anhydride or trifluoroacetic anhydride.

12. A process for the depolymerization of a polyether to a tetrahydrofuran, comprising, contacting at a temperature of about 100°C to about 250°C, a polymer consisting essentially of one or more repeat units of the formula



with a compound of the formula $\text{MZ}_s \cdot \text{Q}_t$, wherein:

each R¹, R², R³ and R⁴ is independently hydrogen or hydrocarbyl containing 1 to 20 carbon atoms;

M is a metal selected from the group consisting of cobalt, vanadium, niobium, tungsten, strontium, barium, scandium, yttrium, the rare earth metals, titanium, zirconium, hafnium, chromium, molybdenum, tantalum, rhenium, iron, ruthenium, osmium, rhodium, iridium, palladium, platinum, silver, gold, zinc, cadmium, mercury, aluminum, gallium, indium, thulium, silicon, germanium, tin, lead, arsenic, antimony and bismuth;

at least one of Z is an anion of the formula $^{-}\text{OSO}_2\text{R}^5$, wherein R^5 is perfluoroalkyl containing 1 to 12 carbon atoms or part of a fluorinated polymer wherein the carbon atoms alpha beta to the sulfonate group are together bonded to at least four fluorine atoms, or tetraphenylborate, and the remainder of Z is oxo or one or more monovalent anions;

s is 2 when M is strontium, barium, cobalt, rhodium, iridium, palladium, platinum, chromium, zinc, cadmium or mercury;

s is 3 when M is scandium, yttrium, a rare earth metal, arsenic, antimony, bismuth, gold, iron, ruthenium, osmium, aluminum, gallium, indium or thulium;

s is 4 when M is titanium, zirconium, hafnium, molybdenum, silicon, germanium, tin, or lead;

s is 5 when M is rhenium, vanadium, niobium or tantalum;

s is 6 when M is tungsten;

Q is a neutral ligand;

t is 0 or an integer of 1 to 6;

and provided that each oxo group present as part of Z is considered to account for two of s.

13. The process as recited in Claim 12 wherein R^1 and R^4 are each hydrogen, and all of R^2 and R^3 are hydrogen.

14. The process as recited in Claim 12 wherein R^1 and R^4 are each hydrogen, one of R^2 is hydrogen, the other R^2 is methyl, and both R^3 are hydrogen.

15. The process as recited in Claim 12 wherein R^5 is trifluoromethyl.

16. The process as recited in Claim 12 wherein said temperature is about 130°C to about 200°C .

17. The process as recited in Claim 12 wherein said compound of formula $\text{MZ}_s\cdot\text{QT}$ is about 1 to about 3% by weight of said polyether.

18. The process as recited in Claim 12 wherein M is strontium, scandium, yttrium, the rare earth metals, titanium, zirconium, hafnium, vanadium, niobium, tantalum, chromium, molybdenum, tungsten, rhenium, iron, ruthenium, palladium, copper, gold, zinc, tin, bismuth or mischmetall.

19. The process as recited in Claim 1 wherein all of Z is an anion of the formula $^{-}\text{OSO}_2\text{R}^5$, and wherein R^5 is trifluoromethyl.

20. The process as recited in Claim 12 wherein all of Z is an anion of the formula $^{-}\text{OSO}_2\text{R}^5$, and wherein R^5 is trifluoromethyl.



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁵ : C08G 65/10, 65/26, 65/32 C07D 307/08	A3	(11) International Publication Number: WO 94/09055 (43) International Publication Date: 28 April 1994 (28.04.94)
(21) International Application Number: PCT/US93/09808 (22) International Filing Date: 20 October 1993 (20.10.93) (30) Priority data: 07/964,313 21 October 1992 (21.10.92) US 08/021,368 23 February 1993 (23.02.93) US 08/093,243 16 July 1993 (16.07.93) US (60) Parent Applications or Grants (63) Related by Continuation US 07/964,313 (CIP) Filed on 21 October 1992 (21.10.92) US 08/021,368 (CIP) Filed on 23 February 1993 (23.02.93) US 08/093,243 (CIP) Filed on 16 July 1993 (16.07.93) (71) Applicant (for all designated States except US): E.I. DU PONT DE NEMOURS AND COMPANY [US/US]; 1007 Market Street, Wilmington, DE 19898 (US).		(72) Inventors; and (75) Inventors/Applicants (for US only) : DRYSDALE, Neville, Everton [JM/US]; 227 Welch Tract Road, Newark, DE 19702-1026 (US). BOCKRATH, Richard, Edmund [US/ US]; 2314 West 17th Street, Wilmington, DE 19806-1331 (US). (74) Agents: GEIGER, Kathleen, W. et al.; E.I. du Pont de Ne- mours and Company, Legal/Patent Records Center, 1007 Market Street, Wilmington, DE 19898 (US). (81) Designated States: JP, KR, US , European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the</i> <i>claims and to be republished in the event of the receipt of</i> <i>amendments.</i> (88) Date of publication of the international search report: 21 July 1994 (21.07.94)
(54) Title: POLYMERIZATION OF, AND DEPOLYMERIZATION TO, CYCLIC ETHERS USING SELECTED METAL COMPOUND CATALYSTS (57) Abstract A process for polymerizing oxiranes, oxetanes, oxepanes, dioxolanes, trioxanes, and tetrahydrofurans to their respective polymers by contacting them with a selected metal compound is disclosed; and also a process for depolymerizing polytetrahydro- furans to monomeric tetrahydrofurans by contacting the polymer with a selected metal compound at a temperature of about 100 °C to about 250 °C.		

INTERNATIONAL SEARCH REPORT

Intern al Application No

PCT/US 93/09808

A. CLASSIFICATION OF SUBJECT MATTER

IPC 5 C08G65/10 C08G65/26 C08G65/32 C07D307/08

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 5 C08G C07D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	POLYMER LETTERS ED., vol.14, 1976 pages 139 - 142 P. DREYFUSS ET AL.: 'Graft copolymers by oxonium polymerization' see page 142, column 9 ---	1-3,7,9, 19
A	FR,A,235 950 (MINNESOTA MINING AND MANUFACTURING CO.) 31 January 1975 see claim 1; table 1 see page 10, line 10 - line 15 see page 14, line 4 - line 5 ---	1-3,7,19
A	WO,A,88 02661 (OLAH G.A.) 21 April 1988 see page 3, line 1 - line 6 see page 10, line 10 - line 13 ---	1-3,7,19
	--- -/--	

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "I" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search

27 May 1994

Date of mailing of the international search report

17. 06. 94

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl.
Fax: (+ 31-70) 340-3016

Authorized officer

Deraedt, G

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

INTERNATIONAL SEARCH REPORT

 Intern. Application No.
 PCT/US 93/09808

C. (Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US,A,4 153 786 (PRUCKMAYR G.) 8 May 1979 see claims 1,3 ---	1,2,4-6, 9-11
A	CHEMICAL ABSTRACTS, vol. 78, no. 16, 23 April 1973, Columbus, Ohio, US; abstract no. 98454j, MATSUKURA K. ET AL.: 'Polyether esters produced by using yttrium catalysts' see abstract & JP,A,7 231 438 (UNITIKA CO. LTD) 14 August 1972 ---	1,3,8
A	US,A,4 115 408 (M.C. BAKER) 19 September 1978 see claims ---	12
A	DATABASE WPI Derwent Publications Ltd., London, GB; AN 87-337120 & JP,A,62 240 319 (MITSUBISHI CHEM. IND. K.K.) 21 October 1987 see abstract ---	12
A	DATABASE WPI Derwent Publications Ltd., London, GB; AN 86-187083 & JP,A,61 120 832 (ASAHI CHEMICAL IND. K.K.) 7 June 1986 see abstract -----	12

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 93/09808

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. Claims: 1-11,19 Polymerisation of cyclic ethers in the presence of selected metal catalysts
2. Claims: 12-18,20 Depolymerisation of polyoxyalkylenes using selected metal catalysts

1. ☒ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☒ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

Information on patent family members

Intern: 31 Application No

PCT-US 93/09808

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
FR-A-235950		NONE	
WO-A-8802661	21-04-88	US-A- 4721559 US-A- 5110778	26-01-88 05-05-92
US-A-4153786	08-05-79	NONE	
JP-A-7231438		NONE	
US-A-4115408	19-09-78	NONE	



This Page Blank (uspto)